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Courier Press, Leamington Spa, England.

## Description

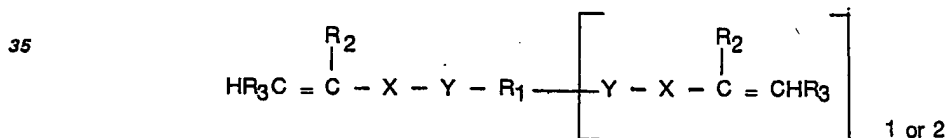
This invention relates to biomedical articles, specially but not exclusively contact lenses, formed from polysiloxane polymers.

- 5 It has now been unexpectedly discovered that by copolymerizing certain polysiloxane monomers, identified below, which contain hydrophilic side chains, with polymerizable comonomers there are formed polymers in a cross-linked network which have advantageous properties which render the polymers useful for forming shaped biomedical articles. More particularly, there may be obtained through the teachings of the present invention contact lenses which are water-absorbing, soft, flexible, hydrolytically stable,  
10 biologically inert, and hydrophilic.

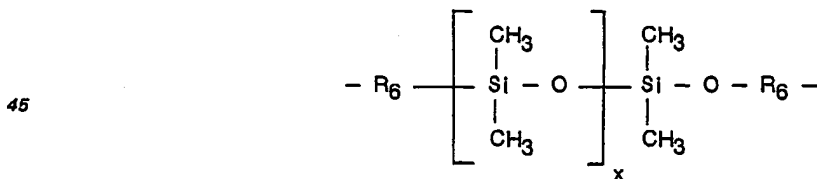
## PRIOR ART STATEMENT

- U.S. patent 4,153,641 teaches contact lenses made from polymers and copolymers comprising poly(organosiloxane) polymers and copolymers formed by polymerizing a poly(organosiloxane) monomer  
15  $\alpha, \omega$  terminally bonded through divalent hydrocarbon groups to polymerized, free radical polymerizably activated, unsaturated groups forming a polymer in a cross-linked network. Additionally, specific comonomers are disclosed which include lower esters of acrylic and methacrylic acid, styryls and N-vinyl pyrrolidinone which may be copolymerized with the above described poly(organosiloxane) monomer to form a copolymer. The preferred polysiloxane monomers of the instant invention include the same  
20 poly(organosiloxane) monomers described above, with the important exception, that the instant polysiloxane monomers additionally contain hydrophilic sidechains. These sidechains result in the polymer formed, being not only hydrophilic, but most importantly water absorbing. Therefore, it was unexpectedly discovered that when the instant polysiloxane monomers, described above, contained hydrophilic sidechains and were copolymerized with certain comonomers, a water absorbing polysiloxane  
25 polymer was formed. This polymer is extremely suitable for making hydrophilic, water absorbing, soft contact lenses. It is generally known in the siloxane art that siloxanes are hydrophobic. There are a few instances where the art teaches hydrophilic polysiloxanes. We know of only one instance, in the prior art, where a polysiloxane is disclosed as being capable of absorbing water. However, this known material as disclosed in U.S. patent 4,136,250 would not be suitable for making contact lens for the reasons stated  
30 herein concerning U.S. 4,136,250 as prior art.

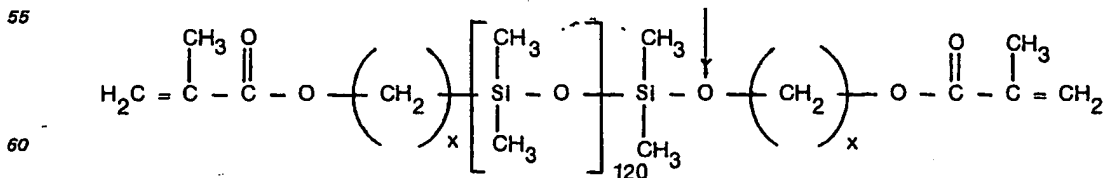
U.S. patent 4,136,250 teaches in pertinent part, a water absorbing polysiloxane which may be used to make soft contact lenses which is obtained by copolymerizing the following siloxane monomer:



- 40 in which  $\text{R}_1$  can be



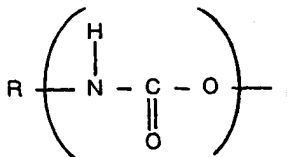
- 50 with a variety of hydrophilic monomers including acrylic acid. The above siloxane monomers can be reduced to a formula similar to but yet critically different from the instant hydrophilic sidechain containing polyorganosiloxane monomers. From the pertinent teachings of U.S. patent 4,136,250 the following siloxane monomer may be derived:



- The oxygen atom in the monomer backbone, with the arrow pointing to it, is present in the '250 formula but not present in the instant hydrophilic sidechain containing polyorganosiloxane monomers.  
65 This oxygen atom presents several problems.

This particular oxygen atom, because of its placement between the silicon and carbon atoms, is subject to hydrolysis and alcoholysis. This bond will hydrolyze, even at room temperature, in the presence of water. Stability is important, if this material is to be used for biomedical devices, such as, contact lenses, since these types of devices are usually heated in water in order to disinfect them. If, during disinfecting the contact lens loses its shape, then it loses its optics. This means that the material taught in '250 would be undesirable for use in certain medical devices including contact lenses. The instant hydrophilic sidechain containing polyorganosiloxane monomers results in copolymers which have superior hydrolytic stability since there is no Si—O—C linkage.

Also to be considered are the examples of '250. Only in these examples of '250 are there specific monomers disclosed without this undesirable Si—O—C linkage. However, these specific monomers have undesirable urethane linkages or couplings which present structures which are even more different from the instant monomers. The urethane linkage, i.e.,



as mentioned, is also undesirable for use in medical devices, particularly contact lenses. However, in addition, the instant hydrophilic sidechain containing polyorganosiloxane monomers have no urethane linkages.

Dutch patent 7,704,136 published 18 October 1977 teaches, in pertinent part, a wettable siloxane material for use in making contact lenses. However, '136 teaches that the wettable contact lenses should not absorb water since water absorption, as taught in '136, would cause water to be discharged into the eye when the contact lenses are in use. This is viewed as a disadvantage in '136. The instant invention in a specific embodiment concerns a hydrophilic side chain containing polysiloxane contact lens which absorbs water in larger amounts. Water absorption is viewed by the instant inventors as an advantage. The Dutch reference '136 further teaches that a lens should not absorb water since, as taught in '136, such a lens would undergo changes, such as, changing its optical properties. '136 further teaches that the handling of such a lens is difficult because, when it is swellable, it is physically weak. However, the instant lenses are made from hydrophilic side chain containing polysiloxane material which is strong, durable, water absorbing and oxygen permeable. The Dutch patent further refers to some of the monomers which may be reacted with the polysiloxanes taught in '136 which are esters of glycidyl alcohol and esters of certain acids including acrylic acid and methacrylic acid. '136 also suggests the use of specific anhydrides such as maleic anhydride. Nowhere does this Dutch reference '136 disclose the instant hydrophilic side chain containing polysiloxanes or that certain comonomers may be reacted with these monomeric hydrophilic side chain containing siloxanes in order to form the instant water absorbing copolymers as disclosed herein.

U.S. patent 3,228,741 teaches, in pertinent part, a silicone contact lens in general. However, nowhere are any hydrophilic sidechains disclosed. Neither does '741 teach a hydrophilic, water absorbing siloxane contact lens as in the instant invention.

U.S. patent 3,700,573 teaches, in pertinent part, radiation grafting of hydrophilic polymers to polysiloxanes. These siloxanes are then used in making contact lens. One skilled in the art would be taught that something must be done to polysiloxanes in order to make them hydrophilic. As taught in '573, silicones are inherently hydrophobic. In '573 the surface is treated in order to make this material hydrophilic. Surface treatment is not as effective as the instant invention for making a siloxane hydrophilic. Surface treatment only affects the surface on the contact lens. This surface can be removed, for example, by abrasion. However, in the instant invention, the siloxane material is hydrophilic throughout. Also, and most importantly, the instant material is water absorbing.

U.S. Patent 3,916,033 teaches, in pertinent part, radiation grafting hydrophilic polymers onto polymethyl siloxane in order to make it hydrophilic. This material is then used to make contact lens. More specifically, '033 teaches using polydimethylsiloxane and radiation grafting onto the surface of this material, N-vinyl-pyrrolidone. As mentioned grafting is not used in the instant invention.

#### SUMMARY OF THE INVENTION

The instant invention provides water absorbing polysiloxane materials which are used for biomedical devices, such as contact lenses, heart valves and intraocular lenses.

The instant invention in a specific embodiment comprises a water absorbing, soft, hydrophilic, flexible, fillerless, hydrolytically stable, biologically inert contact lens with the capability of transporting oxygen sufficiently to meet the requirements of the human cornea. The instant contact lenses and other biomedical devices are prepared from a material, defined with greater particularity hereafter, which comprises a hydrophilic side chain containing polysiloxane monomer  $\alpha, \omega$  terminally bonded through divalent hydrocarbon groups to activated unsaturated groups copolymerized to form a polymer in a crosslinked

network which is capable upon saturation with water of absorbing from about 1 percent to about 99 percent by weight of water, based on the total weight of the polymer and water.

By an "activated unsaturated group" as this term is used herein is meant an unsaturated group which has a multiple unsaturated bond or a pseudo multiple unsaturated bond so as to increase the free radical stability of the double bond through resonance, thereby facilitating free radical polymerization of the monomer. These activated unsaturated groups are polymerized to form the copolymers used in the instant invention. Preferably the activating groups present are such as to lend themselves to polymerization under mild conditions, such as ambient temperatures.

There are commercially available both hydrophobic and hydrophilic contact lenses. The hydrophobic contact lenses available are primarily hard contact lenses made from such material as polymethyl methacrylate (PMMA). However, there are soft contact lenses available which are hydrophilic. Furthermore, these lenses are usually water absorbing lenses and are made from polymers and copolymers based on 2-hydroxyethylmethacrylate (HEMA). However, neither of the materials made from PMMA or PHEMA are oxygen permeable enough to meet all the oxygen requirements of the human cornea. Therefore, a material had to be developed which was soft for comfort and also oxygen permeable to the extent that when the material was made into a contact lens sufficient oxygen would pass through the material to meet all the oxygen requirements of the human cornea. It was found that polysiloxane materials are oxygen permeable to the extent that oxygen will pass through these materials when made into a contact lens sufficiently to meet the requirements of the human cornea. Also, contact lenses made from polysiloxanes are soft resulting in more comfort for the wearer. Therefore, it was found that polysiloxane materials would be good candidates for making soft contact lenses. However, it was found that when soft contact lenses were made from known polysiloxane materials these lenses do not ride on the cornea of the eye on a layer of tears but rather attach themselves to the cornea in a manner which alters the metabolic outflow and inflow of fluid from the eye. It is known that non-movement or substantially non-movement of soft contact lenses on the eye can result in physical damage to the cornea. As mentioned, it has been noted that when a soft contact lens moves on the eye there is also an exchange of tear fluid under the lens resulting in the exchange of metabolic products supplying the cornea and metabolic byproducts being removed from the cornea. This movement of tear fluid results in maintaining a healthy environment for the cornea. This has been generally reported by Roth, H. W. and Iwasaki, W., *Complications Caused by Silicon Elastomer Lenses in West Germany and Japan*, paper presented at the Second Contact Lens Conference, February 18, 1979, in Tokyo, Japan (Prof. Motoichi Itoi, M.D., Kyoto Prefectural University of Medicine, Hirokohji, Kawara Machi-Dori, Kamikyo-Ku, Kyoto 602); Kreiner, Christine F., *Neues Optikerjournal*, No. 2 (21) February 10, 89 (1979); VonArens, Franz D., *Neues Optikerjournal* No. 3, (21) March 10, 93 (1979); and Von Zimmermann E., *Neues Optikerjournal*, No. 4, (21) April 10, 73 (1979).

It was discovered that when a soft contact lens absorbs water and is hydrophilic, that the lens will move on the eye sufficiently so that no physical damage will occur to the cornea and sufficient tear exchange will occur so that corneal metabolism will proceed normally. This has been true when observing the PHEMA lens. The non-movement problem associated with siloxane contact lens has been a major obstacle in preventing the use of polysiloxanes as soft contact lens material. This major obstacle has now been overcome by the instant invention. Therefore, most unexpectedly the instant hydrophilic sidechain containing polysiloxane copolymers are not only hydrophilic but are also water absorbing. Therefore, the instant copolymers make excellent material for manufacturing contact lenses which not only do not stick to the eye but move sufficiently during normal wear so that corneal metabolism will proceed normally.

When the hydrophilic side chain containing polysiloxane monomers of the instant invention are copolymerized with certain comonomers or mixtures thereof disclosed herein, preferably in amounts from about 5.0 percent to about 90.0 percent by weight based on the total weight of the copolymer, a copolymer is formed which is unexpectedly transparent, hydrophilic and water absorbing. When the copolymer is formed into contact lenses, the lenses when saturated with water unexpectedly absorb from about 1 percent to about 99 percent by weight, based on the total weight of the copolymer, of water. This invention is a major advancement in the state of polysiloxane contact lens art. A further advantage of using the instant hydrophilic side chains is that the side chains increase compatibility between comonomers. Therefore, a higher percentage of comonomers may be copolymerized with the siloxane monomers without phase separation, resulting in an optically clear, not a cloudy, product. However, if there is a phase separation, the domains are not large enough to scatter visible light so the product still remains optically clear. This is important since the other comonomers disclosed herein also add to the water absorbing properties of the copolymers formed herein.

The three-dimensional network polymer products of the instant invention are readily prepared by means of conventional polymerization techniques. For example, the monomers together with about 0.05 to about 4.0 percent, preferably 0.05 to 2.0 percent by weight of an appropriate free radical initiator may be heated to a temperature of from about 30°C to about 100°C to initiate and complete the polymerization. The polymerizable monomers can preferably be subjected at room temperature to radiation by UV light in the presence of suitable activators such as benzoin, acetophenone, benzophenone and the like for a sufficient time so as to form a three-dimensional polymer network.

The polymerization can be carried out directly in contact lens molds or can be cast into discs, rods, or sheets which can then be fabricated to a desired shape. Preferably the polymerization is carried out while

the material is being spin cast, such as taught in U.S. patent 3,408,429.

When the term "movable soft contact lens" is used herein it is meant that when the lens is placed on the eye and during normal wear the lens will move at least 0.5 mm with each blink of the eyelid. Preferably the lens should move from about 0.5 mm to about 1.0 mm with each blink.

Further, when the term "movable soft contact lens" is used herein, it is meant that the lens moves sufficiently on the eye so that (1) no physical damage occurs to the cornea and (2) sufficient tear fluid exchange occurs under the lens so that sufficient cornea metabolic activity is maintained resulting in a healthy environment for the cornea.

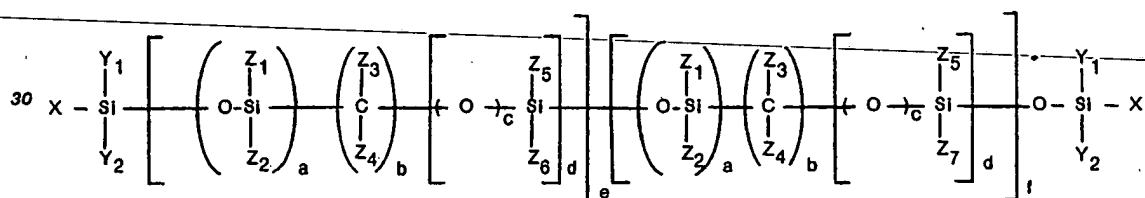
When the term "non-movable soft contact lens" is used herein, it is meant that the lens will move less than about 0.5 mm with each blink of the eyelid.

When the term "hydrophilic soft contact lens" is used herein, it is meant that the soft contact lens surface will not repel water as opposed to the "hydrophobic" where the lens surface will tend to repel water.

When the term "water absorbing soft contact lens" is used herein, it is meant that the lens will absorb from about 1 percent to about 99 percent by weight of water, based on the total weight of the polymer and water.

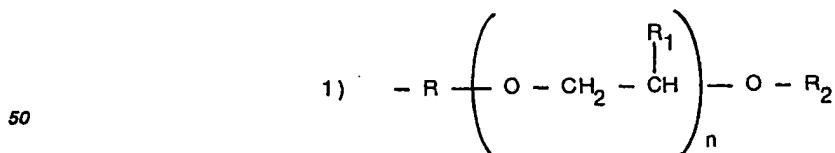
In accordance with this invention shaped articles for use in biomedical applications, including contact lenses, are provided which are fabricated from three-dimensional network copolymers comprising a hydrophilic side chain containing polysiloxane monomer  $\alpha,\omega$  terminally bonded through divalent hydrocarbon groups to activated (as herein defined), unsaturated groups copolymerized with, a comonomer preferably in an amount of from about 5.0 percent by weight to about 90.0 percent by weight based on the total weight of the copolymers, thereby forming a polymer in a crosslinked network capable of absorbing from about 1 percent to about 99 percent by weight of water based upon the total weight of the polymer and water.

The polysiloxane monomers which are used in the instant invention have the following formula:



wherein  $Y_1$  and  $Y_2$  are the same or different and are selected from the group consisting of a hydrocarbon having from 1 to 20 carbon atoms and a halogenated hydrocarbon having from 1 to 20 carbon atoms, X is an activated unsaturated group (as herein defined) bonded through a divalent hydrocarbon group, a is at least 1, b is zero or at least 2, c is 1 if b is zero and c is zero if b is at least 2, d is at least 1, except when b is zero and a is 1 then d is zero or greater, e is at least 1 and f is zero or greater,

$Z_1$  through  $Z_7$  are the same or different and at least one of  $Z_1$  through  $Z_7$  is a hydrophilic sidechain and  $Z_1$  through  $Z_7$  are selected from the group consisting of a monovalent hydrocarbon having from 1 to 20 carbon atoms, a halogenated monovalent hydrocarbon having from 1 to 20 carbon atoms and a hydrophilic sidechain with the following formulas selected from the group consisting of



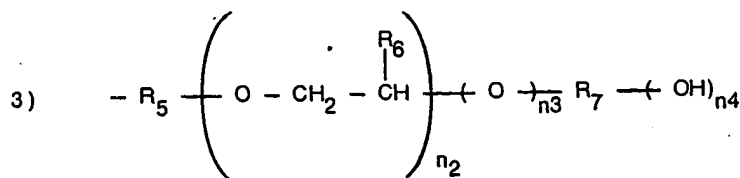
wherein R is a divalent hydrocarbon having from 1 to 10 carbon atoms,  $R_1$  is selected from the group consisting of methyl and hydrogen,  $R_2$  is selected from the group consisting of hydrogen, a monovalent hydrocarbon having from 1 to 10 carbon atoms,



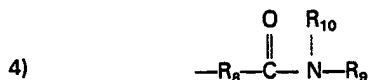
wherein  $R_3$  is selected from the group consisting of a monovalent hydrocarbon having from 1 to 10 carbon atoms and hydrogen, and n is at least 1,



wherein  $R_4$  is a hydrocarbon having from 1 to 20 carbon atoms and a valence of  $n_1 + 1$ ,  $n_1$  is at least 1 and there cannot be an —OH group on an aliphatic carbon atom beta to the Si atom and there can be no more than one oxygen atom on any one carbon atom,



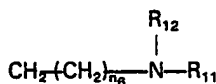
wherein  $R_5$  is a divalent hydrocarbon having from 1 to 10 carbon atoms,  $R_6$  is selected from the group consisting of hydrogen and methyl and  $R_7$  is a hydrocarbon having from 1 to 20 carbon atoms and a valence of  $n_4 + 1$  and can have no more than 1 oxygen atom attached to any one carbon atom,  $n_2$  is zero or greater,  $n_3$  is an integer from zero to 1 and  $n_4$  is at least 1,



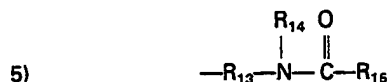
wherein  $R_8$  is a divalent hydrocarbon having from 2 to 10 carbon atoms and the



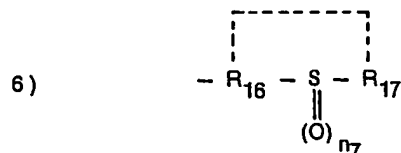
group is not attached to a carbon atom of  $R_8$  which is alpha to the Si atom,  $R_9$  and  $R_{10}$  can be the same or different and are selected from the group consisting of a monovalent hydrocarbon having from 1 to 10 carbon atoms, hydrogen,  $CH_2(CH_2)_{n_5}OH$  wherein  $n_5$  is an integer from 1 to 3 and



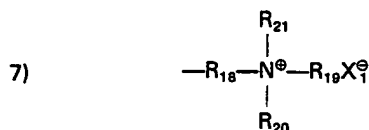
wherein  $R_{11}$  and  $R_{12}$  are the same or different and are selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 10 carbon atoms and  $n_6$  is an integer from 1 to 5,



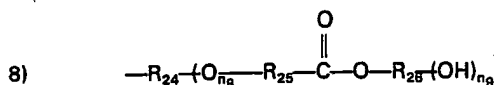
wherein  $R_{13}$  is a divalent hydrocarbon having from 1 to 20 carbon atoms and  $R_{14}$  and  $R_{15}$  are the same or different and are selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 10 carbon atoms,



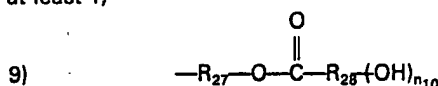
wherein  $R_{16}$  is a divalent or trivalent hydrocarbon having from 1 to 10 carbon atoms and the S atom is not attached to  $R_{16}$  by an aliphatic carbon atom beta to the Si atom,  $R_{16}$  may or may not be attached to  $R_{17}$  to form a ring which contains more than 3 carbon atoms and  $R_{17}$  is selected from the group consisting of a hydrocarbon having from 1 to 10 carbon atoms and  $O^{\ominus} M^{\oplus}$  where M is selected from the group consisting of a monovalent metal ion and a quaternary ammonium ion, and  $n_7$  is an integer from 1 to 2,



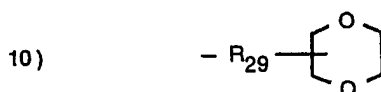
wherein  $R_{18}$  is a divalent hydrocarbon having from 3 to 10 carbon atoms and the  $N^{\oplus}$  must be attached to a carbon atom of  $R_{18}$  which is at least 2 carbon atoms away from the Si atom,  $R_{19}$ ,  $R_{20}$  and  $R_{21}$  are the same or different and are monovalent hydrocarbons having from 1 to 10 carbon atoms,  $X_1^{\ominus}$  is a monovalent anion selected from the group consisting of halides,  $R_{22}-COO^{\ominus}$  wherein  $M_{22}$  is selected from the group consisting of hydrogen, a monovalent hydrocarbon having from 1 to 10 carbon atoms and a halogenated monovalent hydrocarbon having from 1 to 10 carbon atoms and  $R_{23}-SO_3^{\ominus}$  wherein  $R_{23}$  is selected from the group consisting of a monovalent hydrocarbon having from 1 to 10 carbon atoms and a halogenated monovalent hydrocarbon having from 1 to 10 carbon atoms,



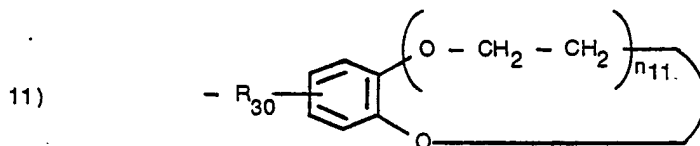
wherein  $R_{24}$  is a divalent hydrocarbon having from 1 to 10 carbon atoms and  $n_8$  is an integer from 0 to 1 and when  $n_8$  is 1 the oxygen cannot be attached to an aliphatic carbon atom in  $R_{24}$  which is beta to the Si atom,  $R_{25}$  is a divalent hydrocarbon having from 1 to 10 carbon atoms,  $R_{28}$  is a hydrocarbon having from 2 to 20 carbon atoms and a valence of  $n_9 + 1$  and can have no more than 1 oxygen atom attached to any one carbon atom and  $n_9$  is at least 1,



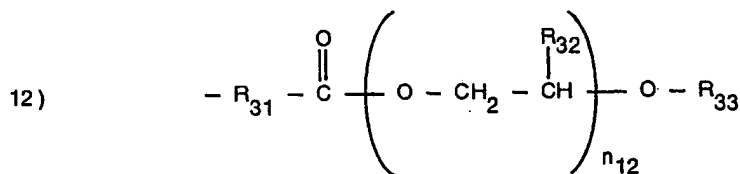
wherein  $R_{27}$  is a divalent hydrocarbon having from 1 to 10 carbon atoms and the oxygen atom bonded to  $R_{27}$  cannot be attached to an aliphatic carbon atom in  $R_{27}$  which is beta to the Si atom,  $R_{28}$  is a hydrocarbon having from 2 to 20 carbon atoms and a valence of  $n_{10} + 1$  and can have no more than 1 oxygen atom attached to any one carbon atom and  $n_{10}$  is an integer of at least 1,



wherein  $R_{29}$  is a divalent hydrocarbon having from 1 to 10 carbon atoms,



wherein  $R_{30}$  is a divalent hydrocarbon having from 0 to 10 carbon atoms and  $n_{11}$  is an integer from 1 to 10,



wherein  $R_{31}$  is a divalent hydrocarbon having from 2 to 10 carbon atoms and the carbonyl group is not attached to a carbon atom alpha to the Si atom,  $R_{32}$  is selected from the group consisting of methyl and hydrogen,  $R_{33}$  is selected from the group consisting of hydrogen, a monovalent hydrocarbon having from 1 to 10 carbon atoms and

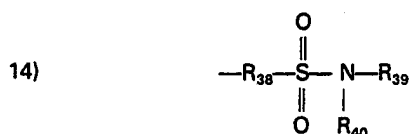


wherein  $R_{34}$  is a monovalent hydrocarbon having from 1 to 10 carbon atoms and  $n_{12}$  is at least 1,

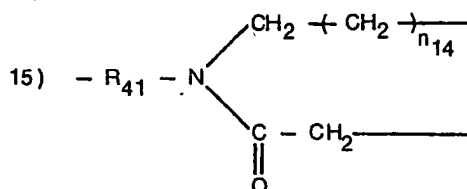


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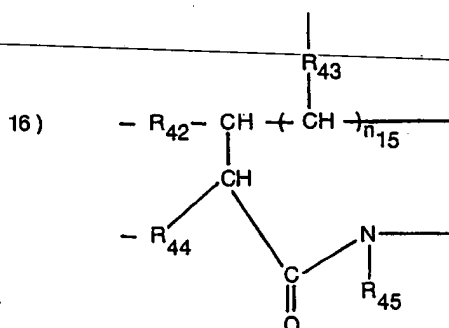
wherein  $R_{35}$  is a divalent hydrocarbon having from 1 to 10 carbon atoms,  $R_{36}$  and  $R_{37}$  can be the same or different and are selected from the group consisting of hydrogen, monovalent hydrocarbons having from 1 to 10 carbon atoms and  $-(CH_2)_{n_{13}}-OH$  where  $n_{13}$  is 2 to 4,



wherein  $R_{38}$  is a divalent hydrocarbon having from 1 to 10 carbon atoms and the S atom cannot be attached to a carbon atom of  $R_{38}$  which is alpha to the Si atom,  $R_{39}$  and  $R_{40}$  can be the same or different and are selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 10 carbon atoms,



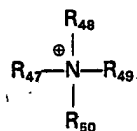
wherein  $R_{41}$  is a divalent hydrocarbon having from 1 to 10 carbon atoms and  $n_{14}$  is an integer from zero to 3,



40 wherein  $n_{15}$  is an integer from zero to 3,  $R_{42}$  and  $R_{43}$  are selected from the group consisting of hydrogen, divalent or monovalent hydrocarbon having from 0 to 10 carbon atoms and  $R_{44}$  is selected from the group consisting of hydrogen, divalent or monovalent hydrocarbon having from 1 to 10 carbon atoms and only one of  $R_{42}$ ,  $R_{43}$  and  $R_{44}$  must be a divalent hydrocarbon and attached to the Si atom,  $R_{45}$  is selected from the group consisting of hydrogen, a monovalent hydrocarbon having from 1 to 10 carbon atoms and  $-(CH_2)_{n_{16}}-OH$  wherein  $n_{16}$  is an integer from 2 to 4,



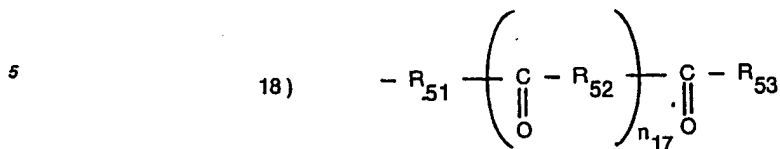
wherein  $R_{46}$  is a divalent hydrocarbon having from 2 to 10 carbon atoms and the carbonyl group cannot be attached to a carbon atom alpha to the Si atom and  $\text{X}_2^{\oplus}$  is a monovalent cation selected from the group consisting of monovalent metal cations and



60 wherein  $R_{47}$ ,  $R_{48}$ ,  $R_{49}$  and  $R_{50}$  are the same or different and selected from the group consisting of hydrogen



and a monovalent hydrocarbon having from 1 to 10 carbon atoms,



10 wherein  $R_{51}$  is a divalent hydrocarbon having from 1 to 10 carbon atoms and the carbonyl group cannot be attached to a carbon atom which is alpha to the Si atom,  $R_{52}$  is a divalent hydrocarbon having from one to 10 carbon atoms,  $R_{53}$  is selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 10 carbon atoms and  $n_{17}$  is an integer from zero to 10, and

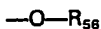


wherein  $R_{54}$  is a hydrocarbon having from 1 to 20 carbon atoms and having a valence of  $n_{18} + 1$  and no  $-\text{C} \equiv \text{N}$  group is attached to a carbon atom of  $R_{54}$  which is alpha to the Si atom and  $n_{18}$  is an integer greater than zero.

20 These polysiloxane monomers are polymerized with comonomers selected from the group consisting of



wherein  $R_{55}$  is selected from the group of hydrogen and methyl and B is selected from the group consisting of



30 wherein  $R_{56}$  is selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 20 carbon atoms,



35 wherein  $R_{57}$  is a hydrocarbon having from 2 to 20 carbon atoms and a valence of  $n_{19} + 1$  and can have no more than one oxygen atom attached to any one carbon atom and  $n_{19}$  is an integer greater than zero,



45 wherein  $R_{58}$  is selected from the group consisting of hydrogen and methyl,  $R_{59}$  is selected from the group consisting of hydrogen, a monovalent hydrocarbon having from 1 to 20 carbon atoms, and



50 wherein  $R_{60}$  is a monovalent hydrocarbon having from 1 to 20 carbon atoms and  $n_{20}$  is an integer greater than zero,

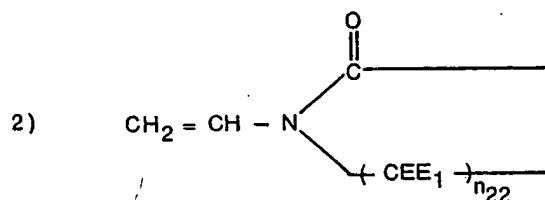


60 wherein  $R_{61}$  and  $R_{62}$  are the same or different and are selected from the group consisting of hydrogen, a monovalent hydrocarbon having from 1 to 20 carbon atoms and  $-(\text{CH}_2)_{n_{21}}-\text{D}$  wherein D is selected from the group consisting of  $-\text{OH}$  and

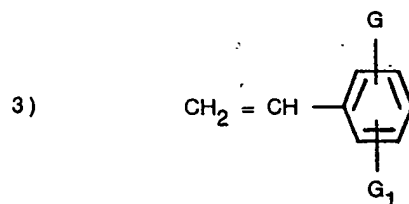


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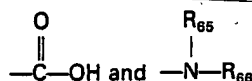
wherein  $R_{63}$  and  $R_{64}$  are the same or different and are hydrogens and monovalent hydrocarbons having from 1 to 20 carbon atoms and  $n_{21}$  is an integer from 2 to 3,



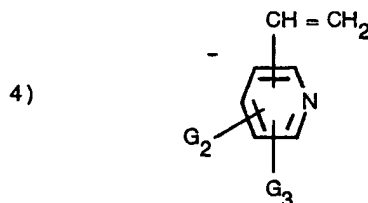
wherein E and  $E_1$  are the same or different and are selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 10 carbon atoms and  $n_{22}$  is an integer from 2 to 5



wherein G and  $G_1$  are the same or different and are selected from the group consisting of hydrogen, a halogen, a monovalent hydrocarbon having from 1 to 20 carbon atoms, hydroxyl,



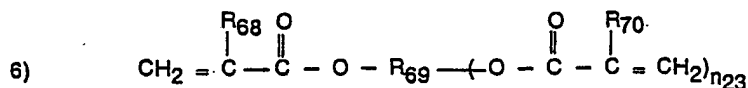
wherein  $R_{65}$  and  $R_{66}$  are the same or different and are selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 20 carbon atoms,



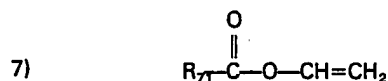
wherein  $G_2$  and  $G_3$  are the same or different and are selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 10 carbon atoms,



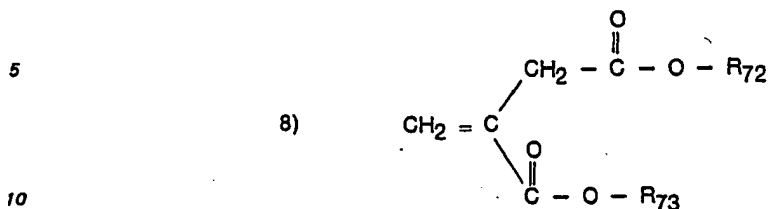
wherein  $R_{67}$  is selected from the group consisting of hydrogen and methyl,



wherein  $R_{68}$  and  $R_{70}$  are the same or different and are selected from the group consisting of hydrogen and methyl,  $R_{69}$  is a hydrocarbon having from 1 to 20 carbon atoms and a valence of  $n_{23} + 1$  and  $n_{23}$  is an integer from 1 to 5,



wherein  $R_{71}$  is a monovalent hydrocarbon having from 1 to 20 carbon atoms and



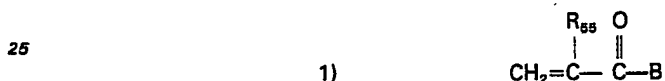
wherein  $R_{72}$  and  $R_{73}$  are the same or different and are selected from the group consisting of hydrogen and monovalent hydrocarbon having from 1 to 20 carbon atoms.

The preferred amount of water absorbed is from about 5.0 percent to about 99 percent by weight, based on the total weight of the polymer and water.

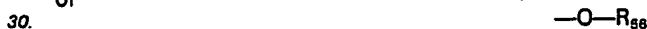
The preferred amount of comonomers, either alone or mixtures thereof, is from about 0.5 percent to about 90.0 percent by weight based on the total weight of the polymers.

The more preferred amount of these comonomers which are used with the hydrophilic sidechain containing polysiloxane monomers herein is from about 0.5 percent to about 70.0 percent by weight based on the total weight of the polymer.

The following are preferred comonomers which may be copolymerized with the instant hydrophilic sidechain containing siloxane monomers disclosed herein to form water absorbing polysiloxane polymers:



wherein  $R_{55}$  is selected from the group of hydrogen and methyl and B is selected from the group consisting of



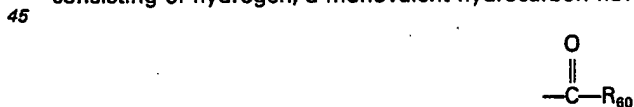
wherein  $R_{56}$  is selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 20 carbon atoms,



wherein  $R_{57}$  is a hydrocarbon having from 2 to 20 carbon atoms and a valence of  $n_{19} + 1$  and can have no more than one oxygen atom attached to any one carbon atom and  $n_{19}$  is an integer greater than zero,



wherein  $R_{58}$  is selected from the group consisting of hydrogen and methyl,  $R_{59}$  is selected from the group consisting of hydrogen, a monovalent hydrocarbon having from 1 to 20 carbon atoms,



wherein  $R_{60}$  is a monovalent hydrocarbon having from 1 to 20 carbon atoms and  $n_{20}$  is an integer greater than zero,



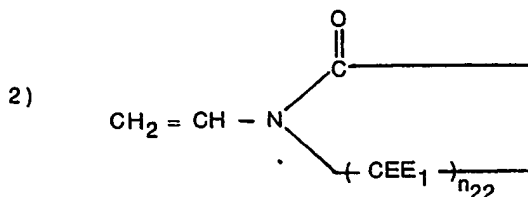
wherein  $R_{61}$  and  $R_{62}$  are the same or different and are selected from the group consisting of hydrogen, a monovalent hydrocarbon having from 1 to 20 carbon atoms and  $-(\text{CH}_2)_{n_{21}}-\text{D}$  wherein D is selected from the group consisting of  $-\text{OH}$  and



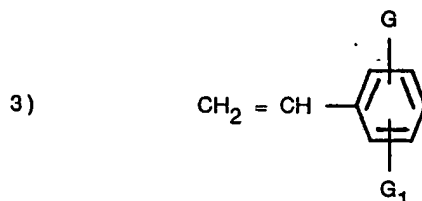
wherein  $R_{63}$  and  $R_{64}$  are the same or different and are hydrogens and monovalent hydrocarbons having

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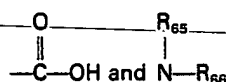
from 1 to 20 carbon atoms and  $n_{21}$  is an integer from 2 to 3,



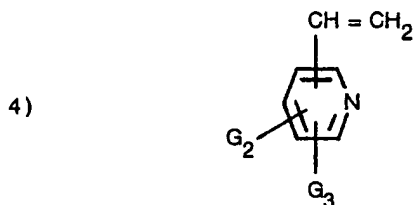
wherein E and  $E_1$  are the same or different and are selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 10 carbon atoms and  $n_{22}$  is an integer from 2 to 5,



wherein G and  $G_1$  are the same or different and are selected from the group consisting of hydrogen, a halogen, a monovalent hydrocarbon having from 1 to 20 carbon atoms, hydroxyl,



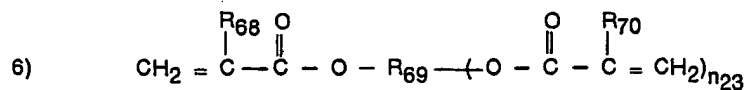
wherein  $R_{65}$  and  $R_{66}$  are the same or different and are selected from the group consisting of hydrogen and a hydrocarbon having from 1 to 20 carbon atoms,



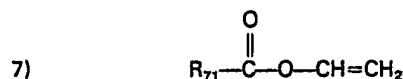
wherein  $G_2$  and  $G_3$  are the same or different and are selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 10 carbon atoms,



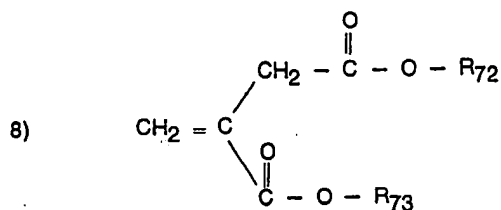
wherein  $R_{67}$  is selected from the group consisting of hydrogen and methyl



wherein  $R_{68}$  and  $R_{70}$  are the same or different and are selected from the group consisting of hydrogen and methyl,  $R_{69}$  is a hydrocarbon having from 1 to 20 carbon atoms and a valence of  $n_{23} + 1$  and  $n_{23}$  is an integer from 1 to 5,

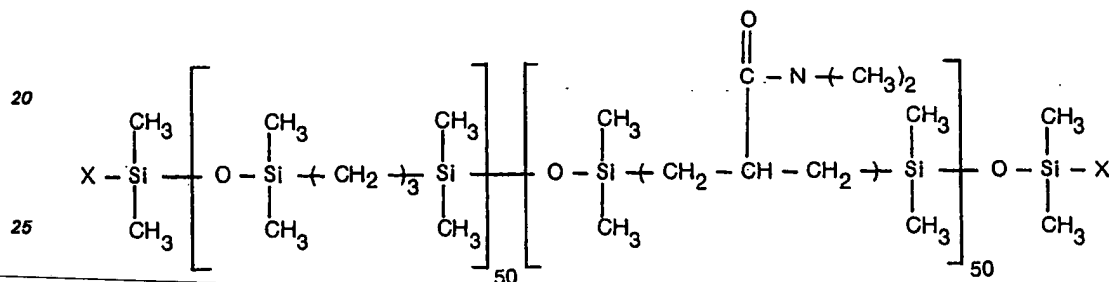


wherein  $R_{71}$  is a monovalent hydrocarbon having from 1 to 20 carbon atoms and

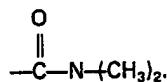


wherein  $R_{72}$  and  $R_{73}$  are the same or different and are selected from the group consisting of hydrogen and monovalent hydrocarbon having from 1 to 20 carbon atoms.

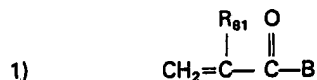
When there are more than one  $Z_1$  on the backbone of the polymer, all of the  $Z_1$ 's may be the same or different. Also, this applies to  $Z_2$  through  $Z_7$ . For example, the following formula is illustrative of this:



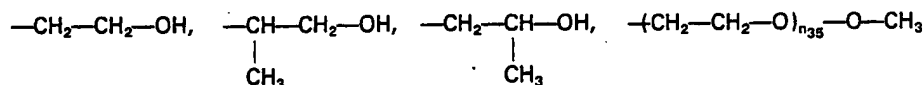
In order to easily locate the  $Z$ 's, compare the above formula with the broad general formula disclosed herein. In the above formula  $Z_1$ ,  $Z_2$ ,  $Z_5$ ,  $Z_6$  and  $Z_7$  equal  $-\text{CH}_3$ , all the  $Z_4$ 's equal hydrogen and there are 250  $Z_3$ 's equal to hydrogen and 50  $Z_3$ 's equal to



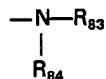
The following are the more preferred comonomers used herein with the instant hydrophilic sidechain containing polysiloxane monomers:



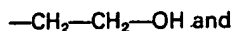
wherein  $R_{81}$  is selected from the group consisting of hydrogen and methyl and B is  $-\text{O}-R_{82}$  wherein  $R_{82}$  is selected from the group consisting of a monovalent hydrocarbon having from 1 to 12 carbon atoms, a monovalent hydrocarbon derivative having from 1 to 12 carbon atoms and hydrogen, and more preferably  $R_{82}$  is selected from the group consisting of hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl and isobutyl,



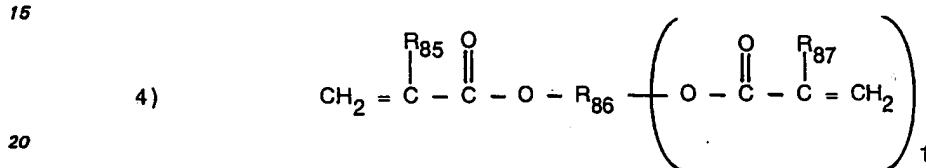
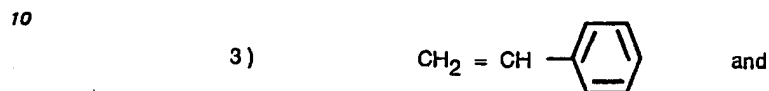
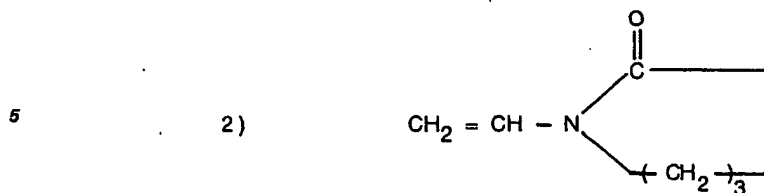
wherein  $n_{35}$  is an integer from 1 to 3,



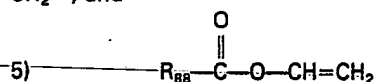
wherein  $R_{83}$  and  $R_{84}$  are the same or different and are selected from the group consisting of hydrogen, methyl and



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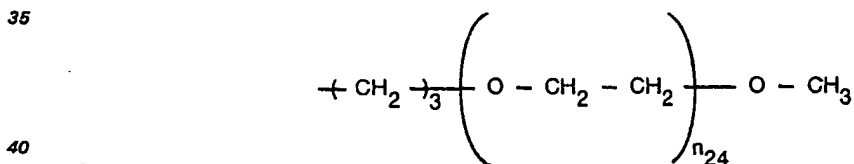
wherein  $R_{85}$  and  $R_{87}$  are the same or different and are selected from the group consisting of hydrogen and methyl and  $R_{86}$  is  $-\text{CH}_2-\text{CH}_2-$ , and



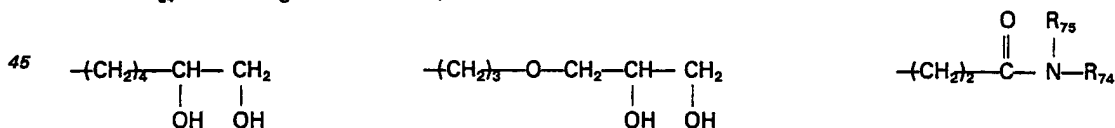
wherein  $R_{88}$  is selected from the group consisting of methyl, ethyl, n-propyl and n-butyl.

30 The following comonomers may also be used. These are polycyclic esters of acrylic and methacrylic acid, isobornyl acrylate, adamantanyl acrylate, dicyclopentadienyl acrylate, menthyl acrylate and isopinocampheyl acrylate.

The preferred hydrophilic sidechains are as follows:



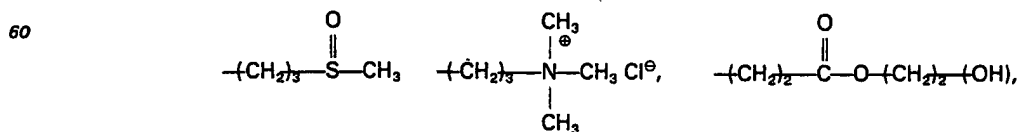
wherein  $n_{24}$  is an integer from 2 to 3,

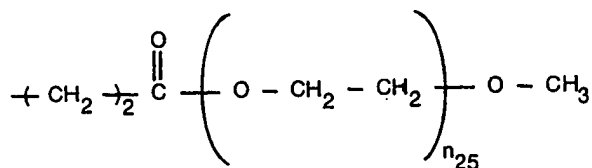


50 wherein  $R_{74}$  and  $R_{75}$  are the same or different and are selected from the group consisting of hydrogen, methyl and  $-\text{CH}_2-\text{CH}_2-\text{OH}$ ,

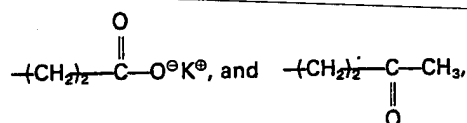
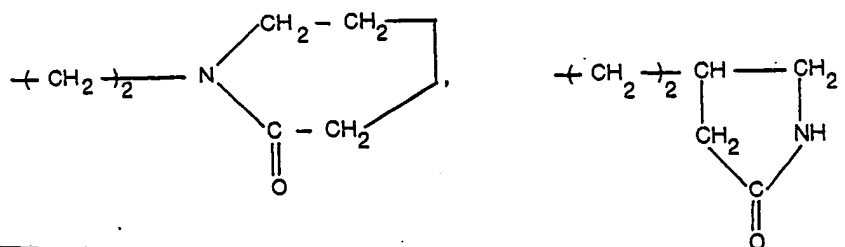
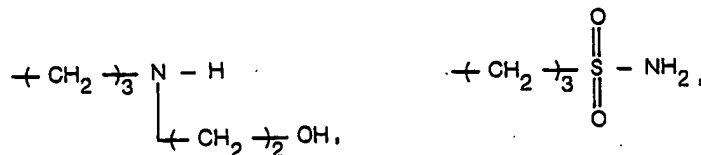


wherein R<sub>76</sub> is selected from the group consisting of hydrogen and methyl,

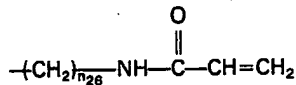




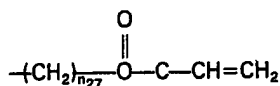
wherein  $n_{25}$  is an integer from 2 to 3



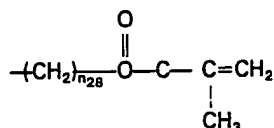
X is preferably the following:



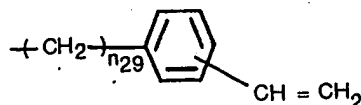
wherein  $n_{26}$  is an integer from 1 to about 10,



wherein  $n_{27}$  is an integer from 1 to about 10,

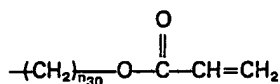


wherein  $n_{28}$  is an integer from 1 to about 10 and



wherein  $n_{29}$  is an integer from 0 to about 10.

X is more preferably:



wherein  $n_{30}$  is an integer from 3 to 4, and



wherein  $n_{31}$  is an integer from 3 to 4,  
X is most preferably:



wherein  $\text{R}_{77}$  is selected from the group consisting of hydrogen and methyl.

Preferably  $\text{Y}_1$  is methyl and  $\text{Y}_2$  is phenyl. Most preferably  $\text{Y}_1$  and  $\text{Y}_2$  are methyls.

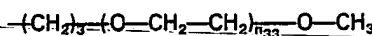
15 Preferably one of  $\text{Z}_1$ ,  $\text{Z}_2$ ,  $\text{Z}_5$  and  $\text{Z}_6$  is a hydrophilic sidechain and a is equal to 1 to about 1,000, b is equal to zero, c is equal to 1, d is equal to 1 to about 1,000, e is equal to 1 and f is equal to zero.

More preferably when only one of  $\text{Z}_1$ ,  $\text{Z}_2$ ,  $\text{Z}_5$  and  $\text{Z}_6$  is a hydrophilic sidechain, a is equal to about 10 to about 500, b is equal to zero, c is equal to 1, d is equal to about 10 to about 500, e is equal to 1, and f is equal to zero.

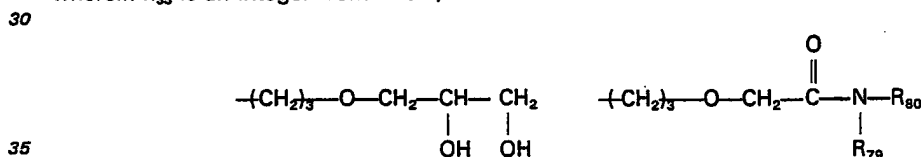
20 Even more preferably when only one of  $\text{Z}_1$ ,  $\text{Z}_2$ ,  $\text{Z}_5$  and  $\text{Z}_6$  is a hydrophilic sidechain a is equal to about 75 to about 150, b is equal to zero, c is equal to one, d is equal to about 25 to about 50, e is equal to one and f is equal to zero.

Most preferably when only one of  $\text{Z}_1$ ,  $\text{Z}_2$ ,  $\text{Z}_5$  and  $\text{Z}_6$  is a hydrophilic sidechain a is equal to about 75, b is equal to zero, c is equal to one, d is equal to about 25, e is equal to one and f is equal to zero.

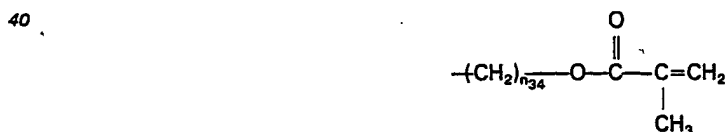
25 Most preferably  $\text{Z}_1$ ,  $\text{Z}_2$  and  $\text{Z}_5$  are methyls and  $\text{Z}_6$  is selected from the group consisting of



wherein  $n_{33}$  is an integer from 2 to 3,



wherein  $\text{R}_{79}$  is selected from the group consisting of methyl and hydrogen,  $\text{R}_{80}$  is selected from the group consisting of methyl, hydrogen and  $\text{---CH}_2\text{---CH}_2\text{---OH}$ ,  $\text{Y}_1$  and  $\text{Y}_2$  equal methyl and X equals



45 wherein  $n_{34}$  is an integer from 3 to 4.

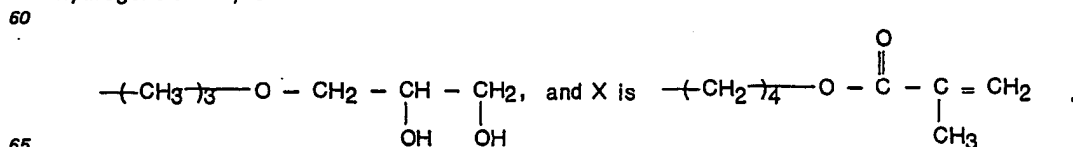
In another preferred embodiment of the instant invention, only one of  $\text{Z}_1$  through  $\text{Z}_7$  is a hydrophilic sidechain and a is equal to one, b is equal to about 2 to about 4, c is equal to zero, d is equal to one, e is equal to about 25 to about 500 and f is equal to about 25 to about 500.

50 In this embodiment, more preferably when only one of  $\text{Z}_1$  through  $\text{Z}_7$  is a hydrophilic sidechain a is equal to one, b is equal to about 2 to about 3, c is equal to zero, d is equal to one, e is equal to about 25 to about 250 and f is equal to about 25 to about 250.

In this same embodiment even more preferably when only one of  $\text{Z}_1$  through  $\text{Z}_7$  is a hydrophilic sidechain a is equal to one, b is equal to about 2 to about 3, d is equal to one, c is equal to zero, e is equal to from about 50 to about 100 and f is equal to from about 50 to about 100.

55 In this same embodiment most preferably when only one of  $\text{Z}_1$  through  $\text{Z}_7$  is a hydrophilic sidechain a is equal to one, b is equal to from about 2 to about 3, c is equal to zero, d is equal to one, e is equal to from about 50 to about 75 and f is equal to from about 50 to about 75.

In this same embodiment also most preferably  $\text{Z}_1$ ,  $\text{Z}_2$ ,  $\text{Z}_5$ ,  $\text{Z}_6$ ,  $\text{Y}_1$  and  $\text{Y}_2$  are methyls,  $\text{Z}_3$  and  $\text{Z}_4$  are hydrogens and  $\text{Z}_7$  is





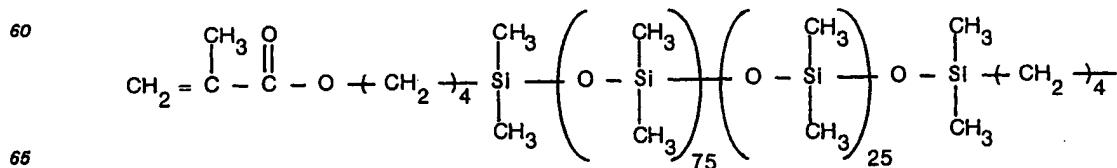
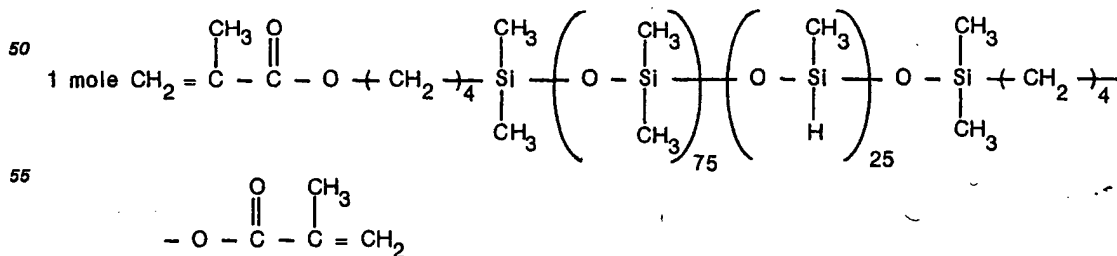
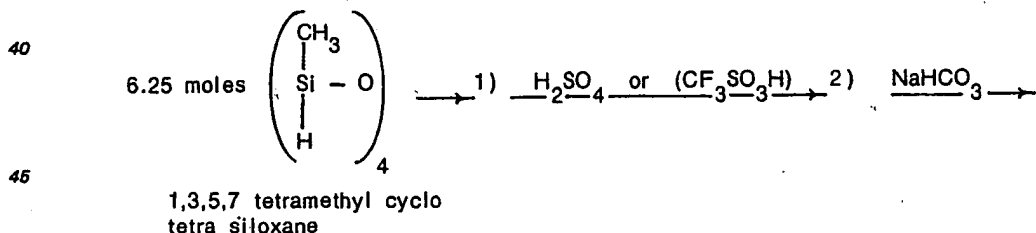
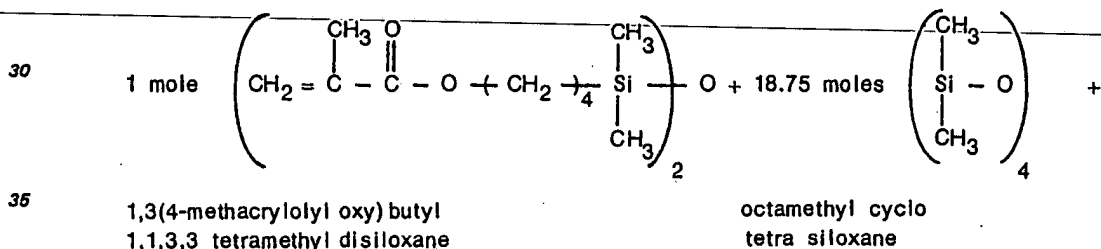
When the statement is made "a polysiloxane monomer  $\alpha,\omega$  terminally bonded through divalent hydrocarbon groups to activated unsaturated groups" it is meant that the hydrophilic sidechain containing polysiloxane monomers as described herein have been attached to a compound having a divalent hydrocarbon group, such as methylene or propylene, etc. and then at each end of this compound is attached an activated unsaturated group such as methacryloxy, etc. and this then is the most preferred hydrophilic sidechain containing polysiloxane monomer. The activated unsaturated groups when polymerized with the defined comonomers form copolymers which are crosslinked.

When the term monomer is used herein with the term polysiloxanes or hydrophilic sidechain containing polysiloxanes, it is meant to include polysiloxanes endcapped with polymerizable unsaturated groups. Preferably these monomers may be poly(organosiloxane) monomers and polyparaffinsiloxane monomers which contain hydrophilic sidechains. The process of lengthening the siloxane portion of the monomer is referred to herein as siloxane ring insertion. The chain length of the polysiloxane center unit of the monomers may be as high as 1,000 or more.

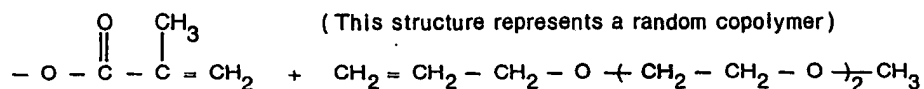
The relative hardness or softness of the contact lenses which represent a preferred embodiment of this invention can be varied by decreasing or increasing the molecular weight of the monomer hydrophilic sidechain containing polysiloxane endcapped with the activated unsaturated groups or by varying the percent and type of the comonomer. As the ratio of siloxane units to endcap units increases, the softness of the material increases. Conversely, as this ratio decreases the rigidity and hardness of the material increases.

As is well established, the oxygen transportability of polysiloxanes is substantially greater in comparison to the conventional contact lens polymers such as polymethyl methacrylate (PMMA) or polyhydroxyethylmethacrylate (PHEMA). The oxygen transportability of the materials of this invention can be varied by altering the percentage of siloxane units in the polysiloxane monomer. For example, a high percentage of siloxane units results in a product more capable of transporting oxygen as compared with a lower percentage of siloxane units which results in a material with less ability to transport oxygen.

The following polysiloxane synthesis and hydrosilation reaction are the most preferred embodiments:



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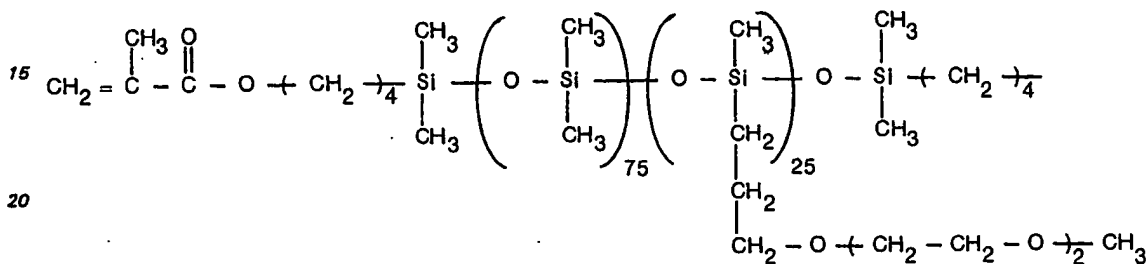
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diethylene glycol allyl methyl ether

Triethylene glycol allyl methyl ether and solketal allyl ether may also be used as preferred replacements for the diethylene glycol allyl methyl ether.

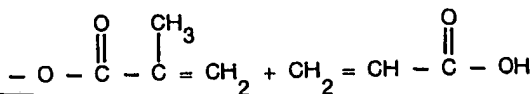
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Pt catalyst



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25



UV initiator or thermal initiator  
forms a three-dimensional copolymer.  
This copolymer is water absorbing.

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Both octamethyl cyclo tetra siloxane and cyclo tetra siloxane are available from Silar Labs, 10 Alplaus Road, Scotia, New York 12302.

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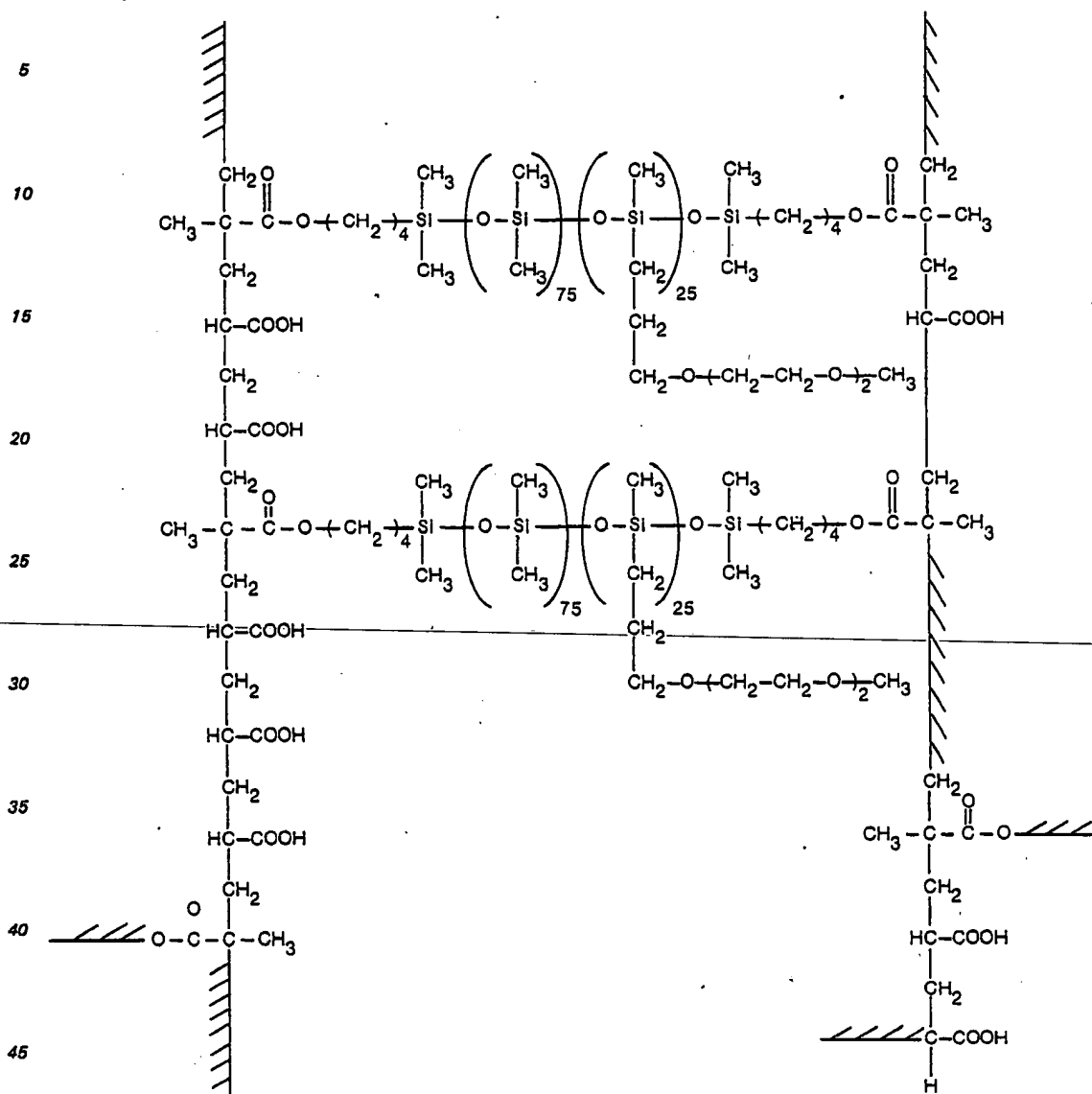
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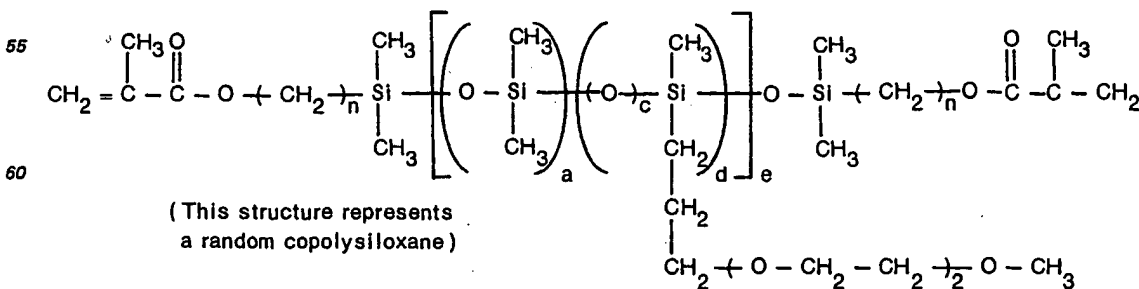
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The following is an example of the three-dimensional network copolymer formed herein:



When the above polymer is made into a contact lens and buffered to pH 7, the contact lens absorbs water. Another important advantage is that with the hydrophilic sidechain one gets increased compatibility between the siloxane and the added comonomers. However, even more importantly the use of the hydrophobic sidechains results in the final product, i.e., the polymer, being more compatible as evidenced by the lack of sufficient scattering of visible light to cause cloudiness.



The Number 75 in the above formula may be replaced by the letter a as shown above. Then a may be 1 to about 1,000, preferably from about 10 to about 500, more preferably from about 75 to about 150 and most preferably 75.

The number 25 in the above formula may be replaced by the letter d as shown above.

Then d may be 1 to about 1,000, preferably from about 10 to about 500, more preferably from about 25 to about 50 and most preferably 25.

The number 4 in the above formula may be replaced by the letter n as shown above.

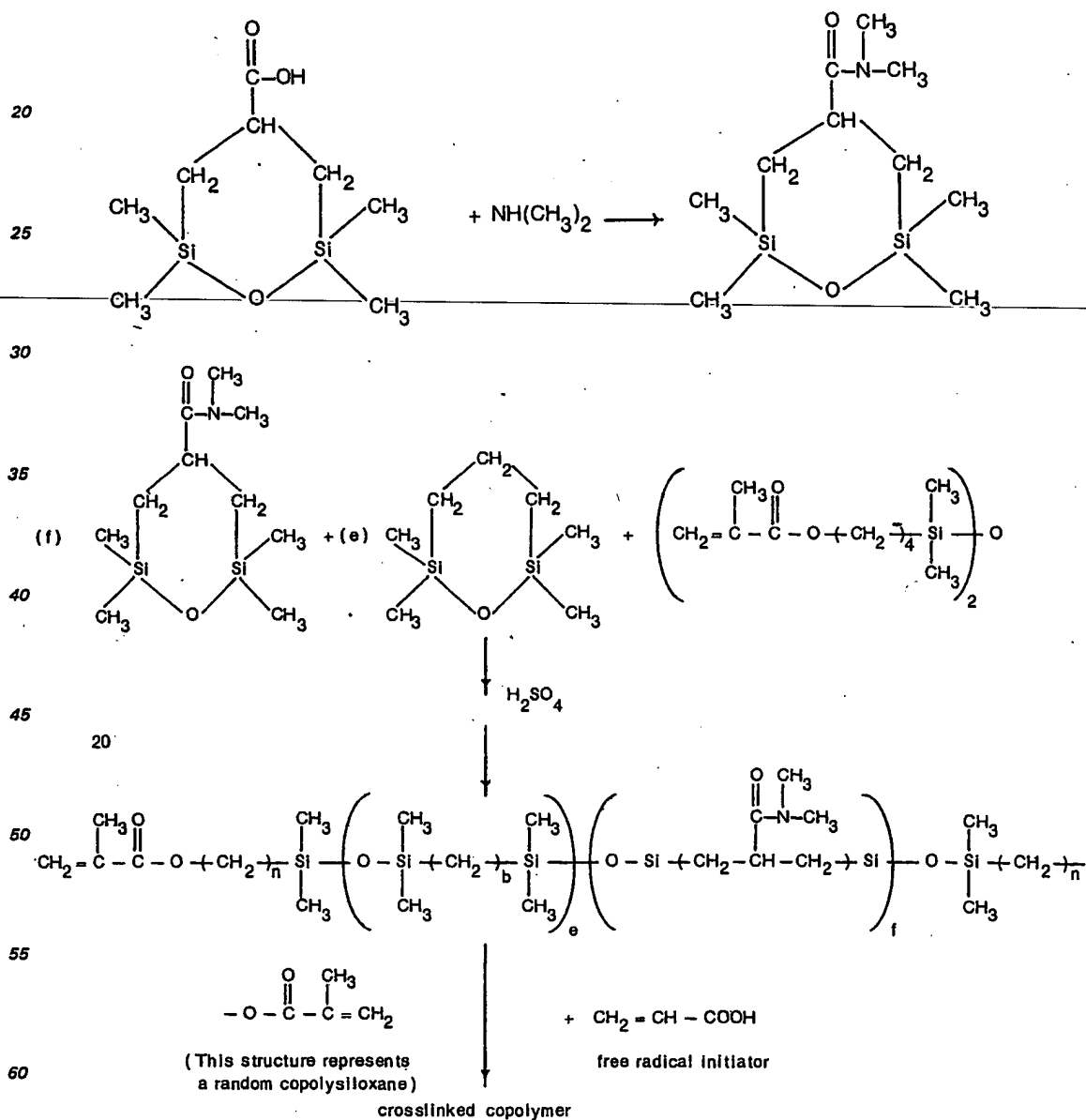
Then n may be from 1 to about 10, preferably 1, 3 or 4 or more preferably about 3 to about 4.

c is always equal to one in the above formula.

e is always equal to one in the above formula.

f is always equal to zero in the above formula.

In another preferred embodiment, the reaction is as follows:



which, after buffering to a pH of 7, is water absorbing. With the hydrophilic sidechain one gets increased

compatibility between the siloxane and the added comonomers and the resulting copolymer is more compatible as evidenced by the lack of scattering of visible light.

In the above formula, e and f may be from about 25 to about 500, preferably from about 25 to about 250, more preferably from about 50 to about 100 and most preferably from about 50 to about 75.

5 In the above formula, b may be from about 2 to about 4 and preferably from about 2 to about 3.

In the above formula, n may be from about 1 to about 10, preferably 1, 3 or 4 and more preferably 3 or 4.

These instant monomers when copolymerized can be readily cured to cast shapes by conventional methods such as UV polymerization, or through the use of free radical initiators plus heat. Illustrative of  
10 free radical initiators which can be employed are bis(isopropyl) peroxydicarbonate, azobisisobutyronitrile, acetyl peroxide, lauroyl peroxide, decanoyl peroxide, benzoyl peroxide, tertiarybutyl peroxyvalate and the like.

In order to further control some of the properties of the copolymers of the instant invention, one can polymerize a mixture of the hydrophilic sidechain containing siloxane monomers having a low value of e  
15 and f with hydrophilic sidechain containing siloxane monomers having a high value for e and f with the comonomers disclosed herein. When e and f in the siloxane monomers have a relatively high value, i.e., above 25, the resulting e.g. contact lenses or other biomedical devices are soft, hydrophilic, water absorbing, oxygen transporting, flexible, hydrolytically stable, biologically inert, transparent, resilient, and do not need fillers to improve the mechanical properties. It is preferred that all the monomers should have  
20 a molecular weight low enough so that the viscosity is low enough to spin cast the monomers, e.g., about  $20 \times 10^{-4}$  m<sup>2</sup>/s or below measured in Gardner viscosity tubes.

The advantages of using the instant copolymers for making soft contact lens are numerous. However, most importantly and unexpectedly the soft contact lens of the instant invention are not only hydrophilic but water absorbing. As mentioned, the art teaches that polysiloxanes are generally hydrophobic. There  
25 are a few exceptions in the art where it is taught that certain polysiloxanes are hydrophilic.

Advantages of using the hydrophilic sidechain containing polysiloxane monomers are (1) polymers made from the hydrophilic sidechain containing polysiloxane monomers, as mentioned, absorb water. As a result of these polymers absorbing water, contact lens made from these water absorbing polymers move  
30 on the eye so that no physical damage will occur to the cornea and sufficient tear exchange will occur so that corneal metabolism will proceed normally. Non-movement and eye damage has been generally associated with siloxane contact lens. (2) The use of the instant hydrophilic sidechains which are attached to the instant siloxane backbones greatly increase the compatibility of the siloxane with the comonomers which are used herein. The use of larger amounts of these other comonomers is desirable since these comonomers also add to the water absorbing properties of the instant copolymers. Even more importantly,  
35 the use of these hydrophilic sidechains results in the final product, i.e., the polymer, being more compatible as evidenced by the lack of sufficient scattering of light to cause cloudiness in the final product. This cloudiness would result in a contact lens made from this material being not optically clear. (3) The advantages of using activated vinyl terminal groups to cure the hydrophilic sidechain containing siloxane monomers permit rapid cure at preferably room temperature if suitable initiators are used. This is desirable  
40 since the preferred method of casting the contact lens is spin casting. (4) No fillers are needed to get useful physical strength as is common with most silicon resins. This is desirable since the use of fillers requires that other possibly undesirable materials be added to the composition in order to match the refractive index of the polymer to that of the filler. (5) Furthermore, the hydrophilic sidechain containing polysiloxane copolymers of the instant invention are oxygen transporting. This is important if the material is to be used  
45 for contact lenses. The human cornea requires  $0.206 \text{ cm}^3/\text{s} \cdot \text{cm}^2 \text{ N/m}^2$  [about  $2 \times 10^{-8} \text{ cm}^3/(\text{sec} \cdot \text{cm}^2 \text{ atm.})$ ] of oxygen through the contact lens as reported by Hill and Fatt, *American Journal of Optometry and Archives of the American Academy of Optometry*, Vol. 47, pg. 50, 1970.

When the terms "oxygen transportability", "oxygen transporting" or "oxygen permeable" are used in the instant application it is meant that the material in the lens will allow sufficient transmission of oxygen  
50 through itself to supply the necessary oxygen requirements of the human cornea and other living tissue. The oxygen requirement for the human cornea, as mentioned is about  $0.206 \text{ cm}^3 \cdot \text{s} \cdot \text{cm}^2 \text{ N/m}^2$  [i.e. about  $2 \times 10^{-8} \text{ cm}^3/(\text{sec} \cdot \text{cm}^2 \text{ atm.})$ ]. The oxygen transportability was determined by a special test procedure described in conjunction with the examples herein. (6) These soft contact lenses are hydrolytically stable, meaning that when the contact lenses or devices are placed into an aqueous solution, e.g., in the eye, or  
55 during the disinfecting step, i.e., water plus heat, the lenses will not change significantly in chemical composition, i.e., hydrolyze and cause the lenses to change shape resulting in an undesirable change in optics. (7) The contact lenses of the instant invention are also resilient. When the term "resilient" is used herein it is meant that after the lenses have been deformed the lenses or devices will return quickly to their original shape. (8) The lenses are preferably made by spin casting, e.g., by the method as disclosed in U.S.  
60 3,408,429. Monomers which have extremely high viscosities may present a problem during spin casting. However, generally the higher the molecular weight of the hydrophilic sidechain containing polysiloxane monomers, the more desirable are the oxygen transporting properties. The longer the chain length and the higher the molecular weight the higher the viscosity of the monomers. However, if spin casting is to be  
65 used the viscosity of the hydrophilic side chain containing polysiloxane monomers must be such that these materials can be spin cast. The hydrophilic side chain containing polysiloxane monomers have viscosities

high enough to give all the desirable properties when polymerized but low enough to be spin cast while still in the monomeric form. The preferred weight average molecular weight is from about 4,000 to 60,000 for the hydrophilic side chain containing polysiloxane monomers of the instant invention. (9) The contact lenses of the instant invention are preferably soft. By the use of the term "soft" in the instant application is meant that the contact lens is capable of being folded or bent back upon itself without breaking.

The most preferred contact lenses of the instant invention, as mentioned, are hydrophilic, water absorbing, have an oxygen transport rate of at least about  $0.206 \text{ cm}^3/\text{s} \cdot \text{cm}^2 \text{ N/m}^2$  are hydrolytically stable, biologically inert, transparent, resilient, and have a softness preferably of about 60 or below on the Shore hardness A scale. Most preferably the Shore hardness should be 25 to 35 on the A scale. To further illustrate the most preferred contact lenses of the instant invention's physical properties, the tensile modulus of elasticity should be about  $500 \text{ g/mm}^2$  or less. If the material is to be used as contact lenses then the Shore hardness and modulus may be related to the comfort of the lenses to the wearer when used on the human eye.

Another advantage of the preferred embodiment, i.e., soft contact lenses, of the instant invention is that lenses made from the copolymers of the instant invention can be made large enough to cover the entire cornea of the eye resulting in more comfort. Hard contact lenses, such as PMMA lenses, have to be made smaller due to their poor oxygen transportability. Furthermore, the larger the lenses, the easier it is to locate the optical center of the lenses. The larger the lens the easier it is to maintain the optical axis which is required in making special lenses, e.g., for those persons with astigmatism. Another advantage of the preferred soft lenses of the instant invention is that the instant preferred soft lenses can have a softness similar to HEMA lenses, but in addition, and most importantly, are more oxygen permeable, i.e., are capable of transporting more oxygen and can be made water absorbing to the same extent as the HEMA lenses. HEMA lenses are oxygen permeable but not oxygen permeable to the extent that the HEMA lenses are capable of transporting oxygen to a degree necessary to meet all the requirements of the human cornea.

Although, as indicated, the copolymers of the instant invention are especially useful for the manufacture of contact lenses, these copolymers can also be employed for other uses, such as other shaped articles for use in biomedical applications. These copolymers can be used to make biomedical devices, i.e., shaped articles, such as, dialyzer diaphragms, to prepare artificial kidneys and other biomedical implants, such as disclosed in Wichterle, U.S. patent 2,976,576 and Wichterle, U.S. 3,220,960. The instant copolymers can also be used in preparing medical surgical devices, e.g., heart valves, vessel substitutes, intrauterine devices, membranes and other films, dialyzer diaphragms, catheters, mouth guards, denture liners and other such devices as disclosed in Shephard U.S. patent 3,520,949 and Shephard U.S. 3,618,231. The instant copolymers can be used to modify collagen to make blood vessels, urinary bladders and other such devices as disclosed in Kliment U.S. patent 3,563,925. The instant copolymers can be used to make catheters as disclosed in Shephard U.S. patent 3,566,874. The copolymers can be used as semipermeable sheets for dialysis, artificial dentures and all of such disclosures as set forth in Stoy U.S. patent 3,607,848. The instant copolymers can be used in ophthalmic prostheses and all other uses disclosed in Wichterle U.S. patent 3,679,504.

When the terms "shaped article for use in biomedical applications" or "biomedical device" are used herein it is meant that the materials disclosed herein have physiochemical properties rendering them suitable for prolonged contact with living tissue, blood or the mucous membrane such as would be required for biomedical shaped articles, such as, surgical implants, blood dialysis devices, blood vessels, artificial ureters, artificial breast tissue and membrane intended to come in contact with body fluid outside of the body, for example, membranes for kidney dialysis and heart/lung machines, and the like. It is known that blood, for example, is rapidly damaged in contact with artificial surfaces. The design of a synthetic surface which is antithrombogenic and non-hemolytic to blood is necessary for prosthesis and devices used with blood. The instant copolymers are compatible with living tissue.

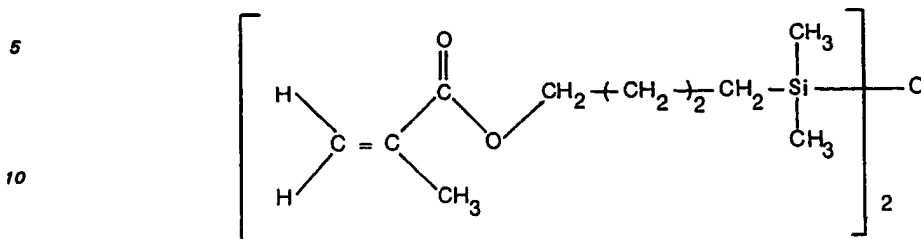
The copolymers disclosed herein can be boiled and/or autoclaved in water without being damaged whereby sterilization may be achieved. Thus, an article formed from the instant copolymers disclosed herein may be used in surgery where an article compatible with living tissue or with the mucous membrane may be used.

The following examples are illustrative only and should not be construed as limiting the invention. All parts and percents referred to herein are on a weight basis and all viscosities measured at 25°C unless otherwise specified.

#### Example I

557 g of 1,3-bis(4-hydroxybutyl)tetramethyl disiloxane, 634 g of dry pyridine and 2 liters of hexane are charged to a 5 liter reaction flask equipped with a mechanical stirrer and drying tube. The mixture is chilled to 0°C and then 836 g of methacryloyl chloride is added dropwise. The mixture is agitated continuously overnight. The reaction solution is extracted consecutively with 10% water solutions of HCl and  $\text{NH}_3$  in order to remove excess reagents and pyridine hydrochloride. The resulting solution of the product in hexane is dried with anhydrous  $\text{MgSO}_4$ , filtered, and solvent removed at reduced pressure. About 459 g (55% yield) of 1,3-bis(4-methacryloxy butyl)tetramethyl disiloxane is collected. The structure is confirmed by infrared spectra, proton magnetic resonance spectra and elemental analysis. IR spectra shows no

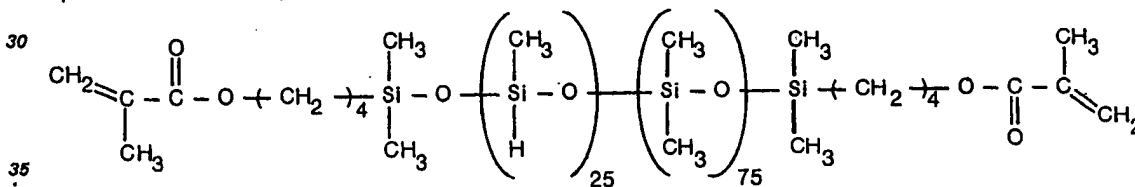
intense hydroxyl band between 3100 and 3600  $\text{cm}^{-1}$  but does show strong methacrylate absorptions at 1640 and 1720  $\text{cm}^{-1}$ . PMR spectra agreed with the proposed structure.



1,3-bis(4-methacryloxy butyl) tetramethyl disiloxane

#### Example II

148.7 g of octamethylcyclotetrasiloxane, available from Silar Labs, 10 Alplaus Road, Scotia, NY 12302, 40.2 g of tetramethylcyclotetrasiloxane, available from Silar Labs, 11.1 g of 1,3-bis(4-methacryloxybutyl) tetramethyl disiloxane as prepared in Example I and 2.0 g of 95%—98%  $\text{H}_2\text{SO}_4$  are charged, under dry air, to a 500 ml 2-neck reaction flask equipped with a mechanical stirrer. The mixture is agitated continuously for 20 hours at which time 17 g of powdered sodium bicarbonate is added to the reaction mixture and stirred for two hours. The resulting mixture is then diluted with 500 ml of hexane, dried over anhydrous  $\text{MgSO}_4$ , filtered and the solvent removed at reduced pressure. The cyclics are removed under high vacuum (6.67 Pa or 0.050 mm) at 60°C for one hour. 180 g of a methacrylate endcapped 25 mole percent silicone hydride polydimethylsiloxane is collected. The polymer is a clear colorless fluid which has a viscosity of 1.1 stokes by Cannon viscometer. The structure is confirmed by infrared spectra, proton magnetic resonance spectra and silicone hydride analysis to be:



The product is a random copolysiloxane.

#### Example III

1,700 ml of dried peroxide free tetrahydrofuran, available from Fisher Scientific Company, 15 Jet View Drive, P.O. Box 8740, Rochester, NY 14624 and 158.7 g potassium metal, available from Fisher Scientific, are charged under dry nitrogen into a 5,000 ml three-neck round bottom flask equipped with mechanical stirrer. The solution is chilled to 10°C, using an icewater bath, and 494 ml of diethylene glycol monomethyl ether, available from Chemical Samples Company, 4692 Kenny Road, Columbus, OH 43221, is added dropwise. The potassium metal reacts within 24 hours at which time 350 ml of allyl chloride available from Aldrich, 159 Forest Street, Metuchen, NJ 08840, is added dropwise at such a rate to maintain a gentle reflux. After the reaction is allowed to continue overnight, one liter of distilled water is added to the reaction vessel to dissolve the precipitated salts. The tetrahydrofuran layer is washed three times with a salt water solution (270 g NaCl to 1 liter  $\text{H}_2\text{O}$ ) to remove excess alcohol. The tetrahydrofuran is removed with a water aspirator and the product is distilled at reduced pressure. 410 g of diethylene glycol allyl methyl ether is obtained (b.p. 109°C/40  $\times 10^2$  Pa). The analytical data is consistent with a product of the general formula:



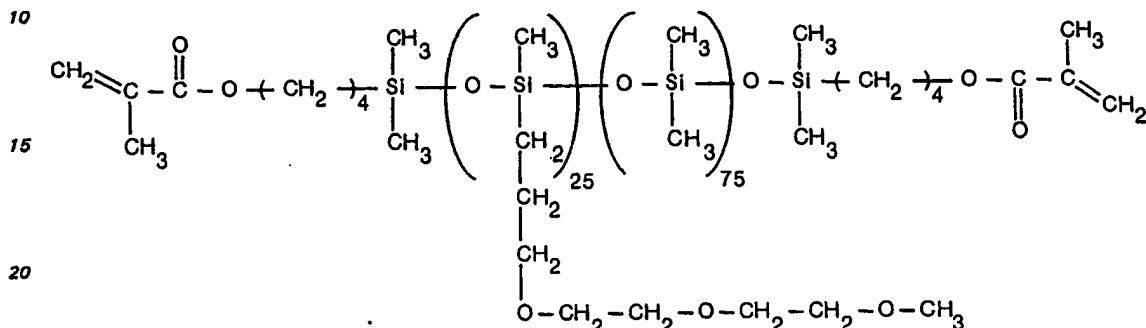
#### Example IV

46.1 g of diethylene glycol allyl methyl ether, as prepared in Example III, followed by 320 ml of hexane, are passed through 42.9 g of activated F-20 alumina, available from Alcoa, Bauxite, AR 72011, into a 1000 ml three-neck flask equipped with mechanical stirrer, thermometer and nitrogen inlet. 40  $\mu\text{l}$  of 20 parts per 1000 Pt solution in the form of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , available from Fisher Scientific, in 2-propanol is added to the mixture. 40 ml of hexane are distilled to remove water and alcohol. The mixture is cooled to 40°C at which time 40 g of methacrylate endcapped 25 mole percent silicone hydride polydimethylsiloxane, as prepared in Example II, is added. Distillation is continued for one hour at which time the temperature is at 80°C. About 200 ml of hexane have been removed. Infrared spectra at 2175  $\text{cm}^{-1}$  shows no remaining silicon hydride band.

The mixture is cooled and diluted with hexane to a total volume of 500 ml. The mixture is divided and

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added to two slurry packed 600 mm x 45 mm fritted silica gel chromatography columns layered with 0.5 cm Celit<sup>®</sup> and 1.5 cm sand. Each column is eluted with 2000 ml of a 1:1 hexane/ether mixture. This fraction contains the excess allylic ether. Each column is then eluted with 2000 ml of a 1:1 hexane/acetone mixture. This fraction contains the polymer. The resulting solution of the product which is in hexane is dried with anhydrous MgSO<sub>4</sub>, filtered and the solvent is removed at reduced pressure. 45 g of a methacrylate endcapped 25 mole percent silicone 3 (diethylene glycol methyl ether) propyl polydimethylsiloxane is obtained. The product is a clear, colorless fluid with a viscosity of  $4.0 \times 10^{-4}$  m<sup>2</sup>/s by Cannon viscometer. Analytical data confirms structure to be:



### Example V

To 72.7 parts of the monomer prepared as in Example IV is added 18.2 parts of isobornyl acrylate, available from Rohm and Haas, Independence Hall West, Philadelphia, PA 19105 and 9.1 parts of acrylic acid and one part diethoxyacetophenone, available from Upjohn, LaPorte, TX-77571. After mixing, a film is cast between glass plates. The film is irradiated with UV light for two hours. The film is released, extracted for four hours in a 1:1 hexane/isopropanol mixture and buffered. This buffering procedure consists of placing the film to be tested, which is about  $5 \times 7.6$  cm in size, into 100 cc of 0.1N ammonium hydroxide for 24 hours. Then the film is soaked in an isotonic phosphate buffer (pH 7.2), i.e.,  $\text{Na}_2\text{HPO}_4$ ,  $\text{NaHPO}_4$  and  $\text{NaCl}$  for another 24 hours. This buffered saline solution is made by mixing 1.403 g of  $\text{Na}_2\text{HPO}_4$ , 0.458 g of  $\text{NaH}_2\text{PO}_4$  and 8.0 g of  $\text{NaCl}$  with water to make a final volume of one liter. The film is then stored in an isotonic buffered saline solution (pH 7.2).

The test procedure for determining the percent of water in the film is as follows:

A 0.3 g sample is taken from the above hydrated film. The sample of film is roller dried and immediately weighed to the nearest milligram. The weighed film is placed into a vacuum oven (1 cm Hg) overnight at 80°C. Then the material is cooled and the vacuum broken by admitting dry air. After the sample is at room temperature for about 15 minutes, the sample is weighed to the nearest milligram. The percent water is calculated as follows:

$$\text{Percent Water} = \frac{\text{Wet Weight} - \text{Dry Weight}}{\text{Wet Weight}} \times 100$$

**The percent water for the above sample is 18%.**

The oxygen permeability of the above sample, in the buffered form, is determined by the following technique:

50 The test is measuring the oxygen permeability of a material while it is wet with the buffered saline solution. This is an attempt to simulate the conditions of a contact lens when on the human eye. Two chambers filled with buffered saline at 32°C are connected together by a common passageway. Across this passageway is placed the material to be tested. The oxygen concentration in the first chamber is lowered by bubbling nitrogen gas into the second chamber until the oxygen concentration in the first chamber is 55 below about 0.1 ppm. Aerated buffered saline (oxygen concentration about 8 ppm) is introduced into the second chamber. There is located in the first chamber an oxygen sensing electrode which measures the oxygen concentration in the first chamber. This measures the oxygen permeability of the material covering the passageway between the two chambers. The oxygen permeability of the sample can be calculated from the rate of oxygen concentration change in the first chamber. The unit of oxygen permeability is

c.c. (S.T.P.) cm  
 Sec. cm<sup>2</sup>mm Hg

65 The oxygen permeability of the above sample is  $6.7 \times 10^{-10}$  cm/sec.cm<sup>2</sup>mmHg or  $8.93 \times 10^8$  cm<sup>3</sup>/



s.cm<sup>2</sup> N/m<sup>2</sup> which is 8.2 times more oxygen permeable than the control material PHEMA, polyhydroxyethylmethacrylate, i.e. HEMA hydr gel.

The following physical properties are measured on an Instron tester ASTM D1708 using standard "dog bone" samples cut from 0.2 mm thick films. This test is used on all the samples where tensile strength, modulus and elongation are measured. The film tested is in the hydrated buffered form.

Tensile Strength — 36 g/mm<sup>2</sup>  
Tensile Modulus — 72 g/mm<sup>2</sup>  
Elongation — 84%

10

#### Example VI

72.7 parts of the monomer as prepared in Example IV are mixed with 18.2 parts of isobornyl acrylate and 9.1 parts of acrylic acid and one part diethoxyacetophenone. 30 µl of the mixture is placed in a suitable contact lens spincoating mold and a contact lens is placed as taught in U.S. patent 3,408,429. After two hours irradiation with UV light, a cured contact lens is obtained. The lens formed is soft, water absorbing, hydrophilic, optically clear, elastic and strong. The lens was worn during clinical testing without trauma for 24 hours by a monkey.

15

#### Example VII

66.7 parts of the monomer as prepared in Example IV are mixed with 16.7 parts isobornyl acrylate and 16.7 parts of acrylic acid and one part diethoxyacetophenone. A film is prepared, extracted and buffered by the procedure as taught in Example V. The percent water of the film is 46%. The film is soft, water absorbing, hydrophilic and optically clear.

20

#### Example VIII

30.8 parts of the monomer as prepared in Example IV is mixed with 7.7 parts isobornyl acrylate and 61.5 parts of acrylic acid and one part diethoxyacetophenone. A film is prepared, extracted and buffered by the same procedure as taught in Example V. The percent water is 84%. The film is soft, water absorbing, hydrophilic and optically clear.

25

#### Example IX

In contrast, 61.5 parts of methacrylate endcapped polydimethylsiloxane as prepared in Example VI of Deichert et al, U.S. patent 4,153,641, is mixed with 15.4 parts isobornyl acrylate and 23.1 parts acrylic acid and one part diethoxyacetophenone. A film is prepared by the same procedure as taught in Example V. Distinct phase separation occurs, as evidenced by the fact that the film is quite cloudy.

30

#### Example X

45.5 parts of the monomer as prepared in Example IV are mixed with 9.1 parts isobornyl acrylate and 45.5 parts hydroxypropylacrylate available from Pfaltz & Bauer, 375 Fairfield Avenue, Stamford, CT 06902, and one part diethoxyacetophenone. A film is prepared by the same procedure as taught in Example V, extracted in 1:1 hexane/isopropanol and hydrated in distilled water for two days. The percent water is measured, using the same procedure as taught in Example V. The percent water is 30%. The film is soft, water absorbing, hydrophilic and optically clear. Physical properties and oxygen permeability are measured also using the same procedure as taught in Example V. The film tested is in the hydrated form.

40

45

Tensile Strength — 54 g/mm<sup>2</sup>  
Tensile Modulus — 68 g/mm<sup>2</sup>  
Elongation — 122%

50

The oxygen permeability is measured in buffered saline and is  $7.3 \times 10^{-10}$  cm<sup>3</sup>/sec-cm<sup>2</sup>-mm Hg or  $9.73 \cdot 10^{-9}$  cm<sup>3</sup>/s.cm<sup>2</sup> N/m<sup>2</sup>, 9 times more oxygen permeable than the control material (PHEMA) polyhydroxyethyl methacrylate.

#### Example XI

In contrast, 80 parts of a methacrylate endcapped polydimethylsiloxane as prepared in Example VI of Deichert et al, U.S. patent 4,153,641 is mixed with 20 parts isobornyl acrylate and 10 parts hydroxypropyl acrylate and one part diethoxyacetophenone. A film is prepared by the same procedure as taught in Example V. Phase separation occurs, as evidenced by the fact that the film is quite cloudy.

55

#### Example XII

50 parts of the monomer as prepared in Example IV is mixed with 50 parts of distilled N-vinyl pyrrolidone available from Aldrich and one part diethoxyacetophenone. A film is prepared and extracted by the same procedure as taught in Example V. The film is hydrated two days in distilled water. The water content is measured also by the same procedure as taught in Example V. The percent of water is 40%. The film is soft, water absorbing, hydrophilic and optically clear.

60

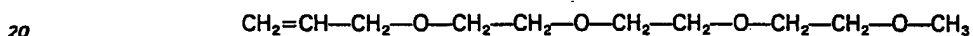
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## Example XIII

100 parts of the monomer as prepared in Example IV is mixed with 60 parts of N,N-dimethyl acrylamide available from Monomer-Polymer & Dajac Laboratories, Inc., 36 Terry Drive, Trevose, PA 19047, and one part diethoxyacetophenone. A film is prepared, extracted and the percent water determined after two days hydration in distilled water by the same procedure as taught in Example V. The water content is 30%. The film is soft, water absorbing, hydrophilic and optically clear.

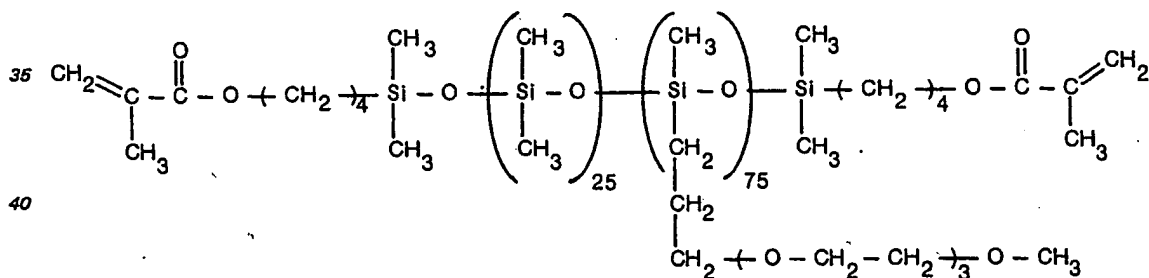
## Example XIV

540 ml of dried peroxide free tetrahydrofuran and 21.5 g of potassium metal are charged into a 2000 ml three-neck flask equipped with mechanical stirrer and a dry nitrogen inlet. 88.4 ml of triethylene glycol monomethyl ether, available from Chemical Samples Co., is added to the mixture dropwise. After the potassium metal has completely reacted, 48.6 ml of allyl chloride is added dropwise to the mixture at such a rate in order to maintain a gentle reflux. After the reaction is complete, 500 ml of distilled water are added in order to dissolve the precipitated salt. The tetrahydrofuran layer is washed with salt water (270 g NaCl/liter water) in order to remove the excess alcohol. The resulting product in tetrahydrofuran is collected and the tetrahydrofuran is removed with a water aspirator. The product is distilled at reduced pressure. 75.5 g (74% yield) of triethylene glycol allyl methyl ether is obtained (b.p. 97°C—100°C/2.66 × 10<sup>2</sup>Pa). The analytical data is consistent with a product of the general formula:



## Example XV

58.8 g of triethylene glycol allyl methyl ether, as prepared in Example XIV, followed by 320 ml of hexane are passed through 54.7 g of activated F-200 alumina into a 1000 ml three-neck flask equipped with mechanical stirrer, thermometer and a dry nitrogen inlet. 40 μl of 20 ppt Pt in 2-propanol is added to the mixture. The mixture is warmed and dried by azeotropic distillation. The mixture is cooled to 40°C at which time 40 g of the methacrylate endcapped 25 mole percent hydride polysiloxane as prepared in Example II is added. Slow distillation is continued for one hour at which time the mixture temperature is 80°C and about 200 ml of hexane have been removed. Infrared spectra shows that the reaction is complete. The polymer is purified by precipitation from a 1:1 mixture of methanol and water. Analytical data confirms the structure to be:

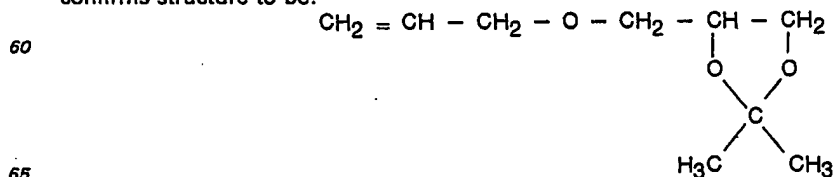


## Example XVI

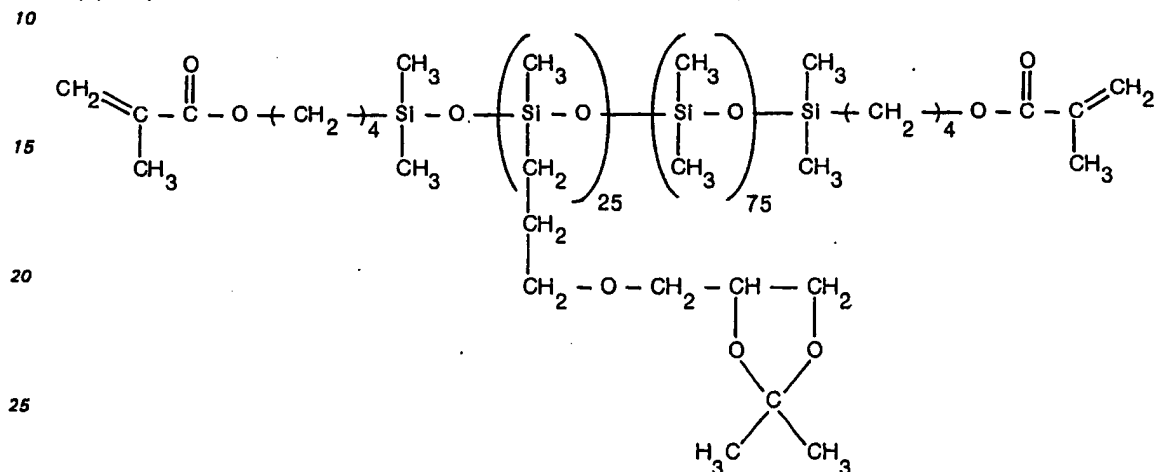
72.7 parts of the monomer prepared in Example XV is mixed with 18.2 parts of isobornyl acrylate and 9.1 parts of acrylic acid and one part diethoxyacetophenone. A film is prepared, extracted and buffered the same as described in Example V. A soft, water absorbing, hydrophilic, optically clear film is obtained.

## Example XVII

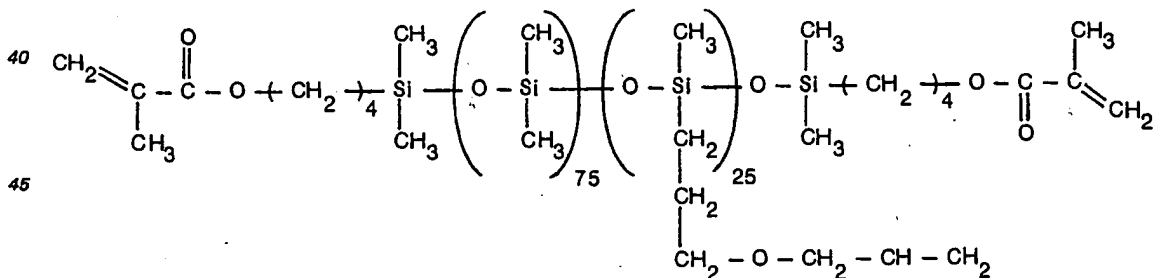
1200 ml of dried peroxide free tetrahydrofuran and 100 g of potassium metal are charged into a 3000 ml three-neck flask equipped with mechanical stirrer, thermometer and a dry nitrogen inlet. 317.7 ml of solketal, available from Aldrich, is added dropwise. After reacting overnight, the potassium metal is reacted completely. 188.5 ml of allyl chloride is added dropwise at such a rate to maintain a gentle reflux. After reacting the mixture again overnight, 850 ml of distilled water are added to dissolve the precipitated salt. The tetrahydrofuran (THF) layer is washed with a salt water solution to remove excess solketal. The resulting product in THF is collected and the THF removed with a water aspirator. The product is distilled at reduced pressure. 261.4 ml of solketal allylether (b.p. 76°C/ 18.67 × 10<sup>2</sup>Pa) is obtained. Analytical data confirms structure to be:



49.5 g of solketalallylether as prepared in Example XVII followed by 320 ml of hexane are passed through 46.1 g of activated F—20 alumina into a 1000 ml three-neck flask equipped with mechanical stirrer, thermometer and a nitrogen inlet. 40  $\mu$ l of 20 ppt Pt in 2-propanol is added to the mixture followed by azeotropic distillation to remove alcohol and water. The charge is cooled to 40°C and 40 g of the methacrylate endcapped 25 mole percent hydride polysiloxane prepared as in Example II is added. Slow distillation continues for one hour during which time the mixture temperature increases to 80°C and about 200 ml of hexane are removed. Infrared spectra confirms the reaction is complete. The polymer is purified by precipitation from a 1:1 mixture of water and methanol. Analytical data confirms the structure to be:



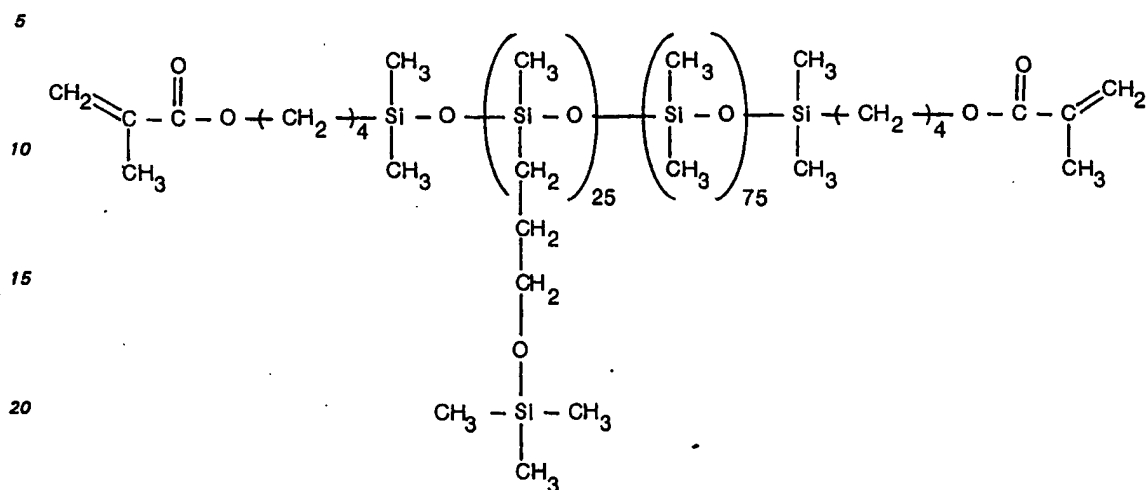
5.0 g of the polymer as prepared in Example XVIII, 52 ml of glacial acetic acid available from Fisher, and 4.2 ml of distilled water are charged to a 100 ml round bottom flask and heated to 50°C overnight at which time the acetic acid and acetone formed during reaction and water are removed under high vacuum. Infrared shows a large hydroxyl bond and the ketal doublet at 1380  $\text{cm}^{-1}$  is gone. The polymer is a clear fluid material or the following structure:



72.7 parts of the polymer as prepared in Example XIX is mixed with 18.2 parts of isobornyl acrylate and 9.1 parts of acrylic acid and one part diethoxyacetophenone. A film is prepared, extracted and buffered as described in Example V. A soft, water absorbing hydrophilic, optically clear film is obtained.

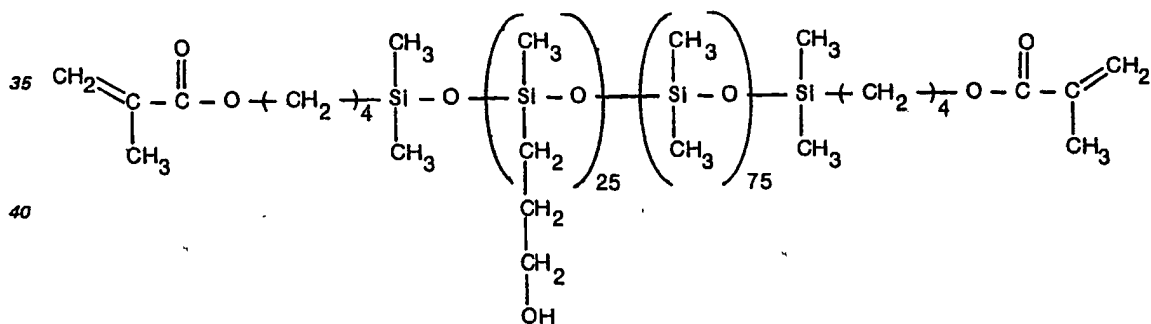
34.9 g of O-trimethylsilyl allyl alcohol available from Petrarch Inc., P.O. Box 141, Levittown, PA 19059, 40  $\mu$ l of 20 ppt Pt in 2-propanol and 320 ml of hexane are charged into a 1000 ml three-neck flask equipped with a mechanical stirrer, a nitrogen inlet and a thermometer. The mixture is warmed to reflux and dried by azeotropic distillation followed by cooling to 40°C. 40 g of the methacrylate endcapped 25 mole percent silicone hydride polysiloxan as prepared in Example II is added. Distillation is continued for one hour during which time the mixture temperature increases to 80°C and about 200 ml of hexane are removed. Infrared spectra confirms that the reaction is complete. The polymer is purified by precipitation from a 1:1

mixture of methanol and water. A clear fluid polymer is obtained having the following structure as confirmed by analytical data:



#### Example XXII

5.0 g of the polymer prepared in Example XXI, 52 ml of glacial acetic acid and 4.2 ml of distilled water are charged to a 100 ml flask and heated to 50°C overnight at which time the acetic acid and water are removed under high vacuum. Infrared shows a large hydroxyl bond. The polymer is a clear fluid material of the following structure:



#### Example XXIII

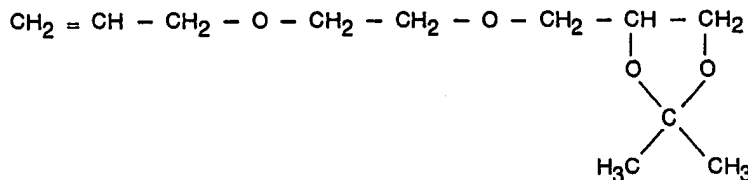
72.7 parts of the polymer as prepared in Example XXII are mixed with 18.2 parts of isobornyl acrylate and 9.1 parts of acrylic acid and one part diethoxyacetophenone. A film is prepared, extracted and buffered as described in Example V. A soft, water absorbing, hydrophilic, optically clear film is obtained.

#### Example XXIV

In a 2 liter, three-necked flask fitted with mechanical stirrer, reflux condensor and a dropping funnel is placed 714 g of 2-allyl oxyethanol available from Haven Chemical Co., 5000 Langdon Street, Philadelphia, PA 19124. 600 g of phosphorous tribromide is added to the mixture dropwise while stirring. This is done over a period of about two hours. The temperature is permitted to rise until the reaction mixture gently refluxes. The mixture is then distilled and the distillate below 160°C is collected in a 2-liter flask with 1 liter of distilled water. The crude 2-allyloxyethylbromide is dried over calcium chloride and distilled. Pure 2-allyloxyethylbromide is obtained.

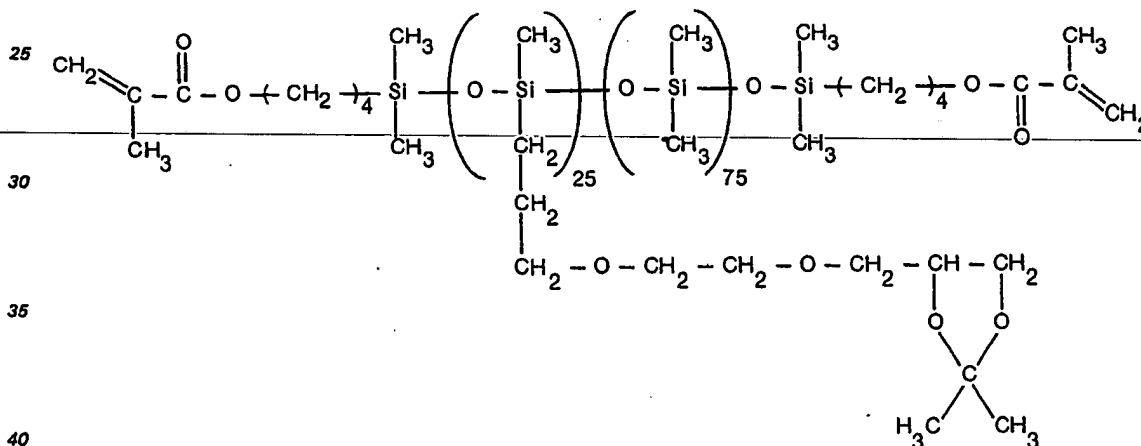
750 ml of dried peroxide free tetrahydrofuran and 14.9 g of potassium metal are charged under dry nitrogen into a 2000 ml three-neck flask equipped with mechanical stirrer, condensor and an addition funnel. 55 g of solketal is added dropwise. Potassium metal reacts completely within 24 hours at which time 68.9 g of the 2-allyloxyethylbromide is added at such a rate as to maintain a gentle reflux. After an overnight reaction, 500 ml of distilled water are added to the reaction vessel to dissolve the precipitated

salts. The THF is then removed with a water aspirator. The product is distilled at a reduced pressure. Pure 2-allyloxyethyl solketal is obtained. Analytical data confirms structure to be:



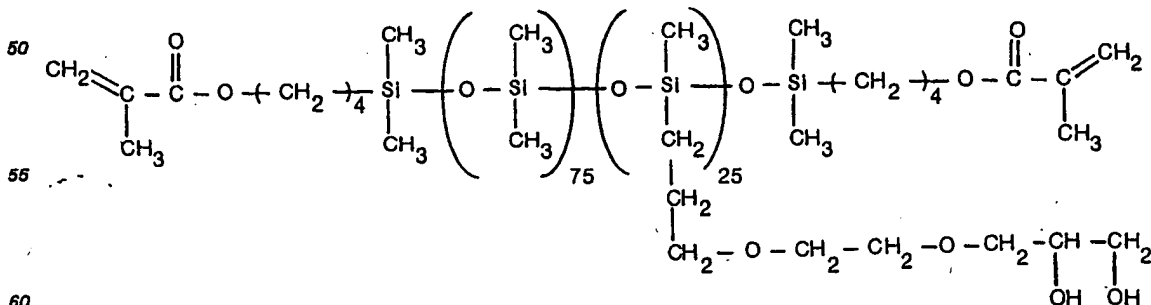
#### Example XXV

62.2 g of the 2-allyloxyethylsolketal as prepared in Example XXIV followed by 320 ml of hexane is passed through 57.9 g of activated F-20 alumina into a three-neck flask equipped with mechanical stirrer and a dry nitrogen inlet. 40  $\mu\text{l}$  of 20 ppt Pt in 2-propanol is added to the mixture. 40 ml of hexane are distilled to remove water and alcohol. The mixture is cooled to 40°C, at which time 40 g of the methacrylate endcapped hydride polydimethylsiloxane as prepared in Example II is added. Distillation is continued for one hour at which time the mixture temperature is 80°C. About 200 ml of hexane are removed. Infrared spectra at 2175  $\text{cm}^{-1}$  confirms the reaction is complete. The polymer is purified by precipitation from a 1:1 methanol/water mixture. A clear fluid polymer is obtained. Analytical data confirms the structure to be:



#### Example XXVI

5.0 g of the polymer as prepared in Example XXV, 52 ml of glacial acetic acid and 4.2 ml of distilled water are charged to a 100 ml flask and heated to 50°C overnight. Then the acetic acid, water and acetone formed are removed under high vacuum. Infrared shows a large hydroxyl band and the ketal doublet at 1380  $\text{cm}^{-1}$  is gone. A clear fluid material of the following structure is obtained:



#### Example XXVII

72.7 parts of the polymer as prepared in Example XXVI is mixed with 18.2 parts of isobornyl acrylate and 9.1 parts of acrylic acid and one part diethoxyacetophenone. A film is prepared, extracted and buffered the same as described in Example V. A soft, water absorbing, hydrophilic, optically clear film is obtained.

## Example XXVIII

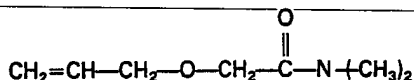
163.3 g of allyl alcohol available from Aldrich in one liter of toluene is charged under dry nitrogen to a 5-liter three-necked flask fitted with a mechanical stirrer and a reflux condenser. 100 g of potassium metal are added, stirring begins and the charge is heated in an oil bath until the mixture refluxes gently.

After the reaction mixture has refluxed for 15 hours, the temperature of the oil bath is lowered to 85°C–90°C, at which time a warm solution of 95 g of monochloroacetic acid in 800 ml of toluene is added at such a rate to maintain a gentle reflux. A precipitate of potassium chloroacetate forms. After all the chloroacetic acid is added the mixture is refluxed and stirred for 48 hours.

When the reaction is complete, the flask is cooled and the reaction mixture is transferred to a 5-liter separatory funnel and extracted with three one-liter portions of water. The water extract is acidified with 20% HCl. The crude allyloxyacetic acid that is produced is extracted three times with ether. The ether extracts are combined and the solvent removed by distillation on a steam bath. The residue is then fractionally distilled under reduced pressure. Pure allyloxyacetic acid is obtained.

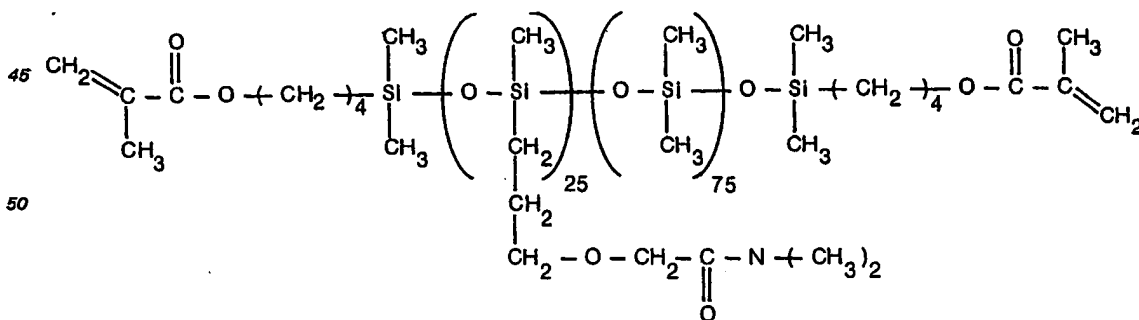
200 g of thionyl chloride is charged to a one-liter three-neck flask equipped with a 250 ml dropping funnel, an efficient condenser and a mechanical stirrer. To this mixture is added dropwise and with rapid stirring, 116 g of allyloxyacetic acid. An evolution of hydrogen chloride and sulfur dioxide takes place. When all the acid has been added, the mixture is heated to 80°C and kept at this temperature for two hours. Then the remaining thionyl chloride is removed on steam bath under reduced pressure. The crude acid chloride is obtained.

In a one-liter flask, equipped with mechanical stirrer and a 500 ml dropping funnel and surrounded by an ice salt freezing mixture, is placed 0.5 l of 28% cold, concentrated aqueous dimethylamine available from Aldrich. The crude acid chloride is added to this mixture slowly while stirring. Stirring is continued for one hour after the addition of the acid chloride. The aqueous mixture is extracted three times with 250 ml of diethyl ether in order to collect the amide which forms. The collected ether is removed by heating the mixture on a steam bath. Then the product is fractionally distilled at reduced pressure. Pure allyloxy N,N-dimethylacetamide is obtained. Analytical data confirms the structure to be:



## Example XXIX

41.1 g of the allyloxyacetamide as prepared in Example XXVIII followed by 320 ml of hexane are passed through 38.3 g of activated F-20 alumina into a 1000 ml three-neck round bottom flask equipped with mechanical stirrer and a nitrogen inlet. 40 µl of 20 ppt Pt in 2-propanol is added to the mixture followed by azeotropic distillation in order to remove water and alcohol. The mixture is cooled to 40°C at which time 40 g of the methacrylate endcapped 25 mole percent silicone hydride polydimethylsiloxane as prepared in Example II is added to the mixture. Distillation continues for one hour during which time the mixture temperature is increased to 80°C resulting in about 200 ml of hexane being removed. Infrared spectra confirms the reaction is complete. The polymer is purified by precipitation from a 1:1 mixture of water and methanol. Analytical data confirms the structure to be:



## Example XXX

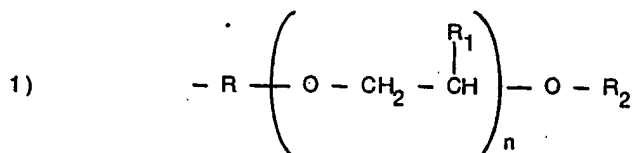
72.7 parts of the polymer as prepared in Example XXIX are mixed with 18.2 parts of isobornyl acrylate and 9.1 parts of acrylic acid and one part diethoxyacetophenone. A film is prepared, extracted and buffered as described in Example V. A soft, water absorbing, hydrophilic, optically clear film is obtained.

## Example XXXI

218 g (1.0 mole) of 1,1,3,3-tetramethyl-1,3-disila-2-oxacyclohexan-5-carboxylic acid (synthesized according to the procedure of Omr W. Steward and Leo H. Sommer, *J. of Organic Chem.*, vol. 26, pg. 4132, [1961]), in 1000 ml of anhydrous tetrahydrofuran, cooled to –15°C, is added (under anhydrous conditions) 101 g of triethylamine and 108.5 g of ethyl chloroformate. After stirring for 15 minutes, dimethylamine is



$Z_1$  through  $Z_7$  are the same or different and at least one of  $Z_1-Z_7$  is a hydrophilic sidechain and  $Z_1$  through  $Z_7$  are selected from the group consisting of a monovalent hydrocarbon having from 1 to 20 carbon atoms, a halogenated monovalent hydrocarbon having from 1 to 20 carbon atoms and a hydrophilic sidechain with the following formulae selected from the group consisting of



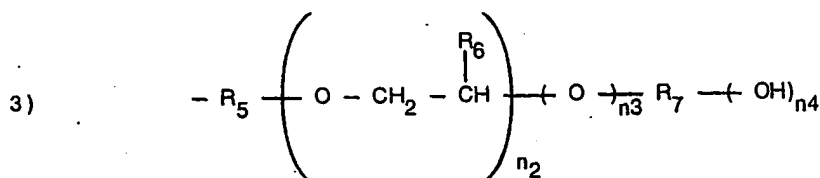
wherein  $R$  is a divalent hydrocarbon having from 1 to 10 carbon atoms,  $R_1$  is selected from the group consisting of methyl and hydrogen,  $R_2$  is selected from the group consisting of hydrogen, a monovalent hydrocarbon having from 1 to 10 carbon atoms,



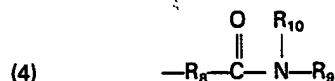
wherein  $R_3$  is selected from the group consisting of a monovalent hydrocarbon having from 1 to 10 carbon atoms and hydrogen, and  $n$  is at least 1,



wherein  $R_4$  is a hydrocarbon having from 1 to 20 carbon atoms and a valence of  $n_1 + 1$ ,  $n_1$  is at least 1 and there cannot be an  $-OH$  group on an aliphatic carbon atom beta to the Si atom and there can be no more than one oxygen atom on any one carbon atom,



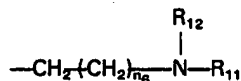
wherein  $R_5$  is a divalent hydrocarbon having from 1 to 10 carbon atoms,  $R_6$  is selected from the group consisting of hydrogen and methyl and  $R_7$  is a hydrocarbon having from 1 to 20 carbon atoms and a valence of  $n_4 + 1$  and can have no more than 1 oxygen atom attached to any one carbon atom,  $n_2$  is zero or greater,  $n_3$  is an integer from zero to 1 and  $n_4$  is at least 1,



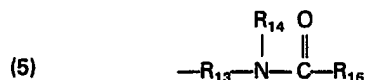
wherein  $R_8$  is a divalent hydrocarbon having from 2 to 10 carbon atoms and the



group is not attached to a carbon atom of  $R_8$  which is alpha to the Si atom,  $R_9$  and  $R_{10}$  can be the same or different and are selected from the group consisting of a monovalent hydrocarbon having from 1 to 10 carbon atoms, hydrogen,  $-CH_2-(CH_2)_{n_5}-OH$  wherein  $n_5$  is an integer from 1 to 3 and

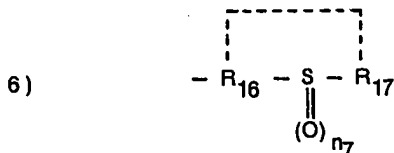


wherein  $R_{11}$  and  $R_{12}$  are the same or different and are selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 10 carbon atoms and  $n_6$  is an integer from 1 to 5,

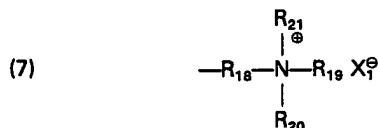




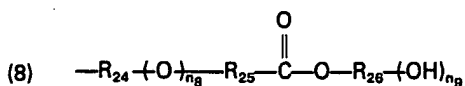
wherein  $R_{13}$  is a divalent hydrocarbon having from 1 to 20 carbon atoms and  $R_{14}$  and  $R_{15}$  are the same or different and are selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 10 carbon atoms,



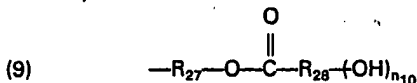
wherein  $R_{16}$  is a divalent or trivalent hydrocarbon having from 1 to 10 carbon atoms and the S atom is not attached to  $R_{16}$  by an aliphatic carbon atom beta to the Si atom,  $R_{16}$  may or may not be attached to  $R_{17}$  to form a ring which contains more than 3 carbon atoms and  $R_{17}$  is selected from the group consisting of a hydrocarbon having from 1 to 10 carbon atoms and  $\text{---O}^\ominus \text{M}^\oplus$  where M is selected from the group consisting of a monovalent metal ion and a quaternary ammonium ion, and  $n_7$  is an integer from 1 to 2,



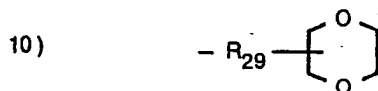
wherein  $R_{18}$  is a divalent hydrocarbon having from 3 to 10 carbon atoms and the  $\text{N}^\oplus$  must be attached to a carbon atom of  $R_{18}$  which is at least 2 carbon atoms away from the Si atom,  $R_{19}$ ,  $R_{20}$  and  $R_{21}$  are the same or different and are monovalent hydrocarbons having from 1 to 10 carbon atoms,  $\text{X}_1^\ominus$  is a monovalent anion selected from the group consisting of halides,  $R_{22}\text{---COO}^\ominus$  wherein  $R_{22}$  is selected from the group consisting of hydrogen, a monovalent hydrocarbon having from 1 to 10 carbon atoms and a halogenated monovalent hydrocarbon having from 1 to 10 carbon atoms and  $R_{23}\text{---SO}_3^\ominus$  wherein  $R_{23}$  is selected from the group consisting of a monovalent hydrocarbon having from 1 to 10 carbon atoms and a halogenated monovalent hydrocarbon having from 1 to 10 carbon atoms,



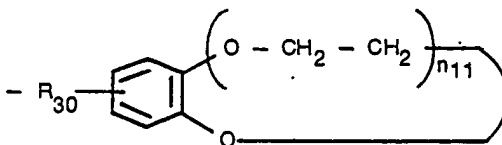
wherein  $R_{24}$  is a divalent hydrocarbon having from 1 to 10 carbon atoms and  $n_8$  is an integer from 0 to 1 and when  $n_8$  is 1 the oxygen cannot be attached to an aliphatic carbon atom in  $R_{24}$  which is beta to the Si atom,  $R_{25}$  is a divalent hydrocarbon having from 1 to 10 carbon atoms,  $R_{26}$  is a hydrocarbon having from 2 to 20 carbon atoms and a valence of  $n_9 + 1$  and can have no more than 1 oxygen atom attached to any one carbon atom and  $n_9$  is at least 1,



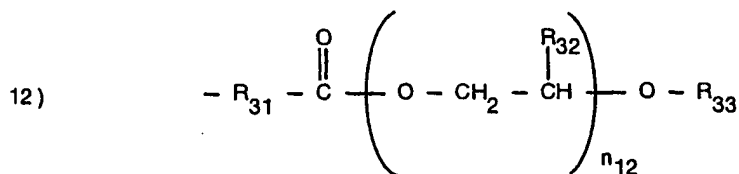
wherein  $R_{27}$  is a divalent hydrocarbon having from 1 to 10 carbon atoms and the oxygen atom bonded to  $R_{27}$  cannot be attached to an aliphatic carbon atom in  $R_{27}$  which is beta to the Si atom,  $R_{28}$  is a hydrocarbon having from 1 to 20 carbon atoms and a valence of  $n_{10} + 1$  and can have no more than 1 oxygen atom attached to any one carbon atom and  $n_{10}$  is an integer of at least 1,



wherein  $R_{29}$  is a divalent hydrocarbon having from 1 to 10 carbon atoms,



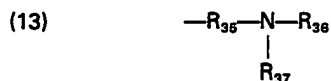
wherein  $R_{30}$  is a divalent hydrocarbon having from 0 to 10 carbon atoms and  $n_{11}$  is an integer from 1 to 10,



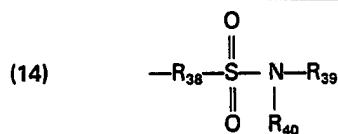
10 wherein  $R_{31}$  is a divalent hydrocarbon having from 2 to 10 carbon atoms and the carbonyl group is not attached to a carbon atom alpha to the Si atom,  $R_{32}$  is selected from the group consisting of methyl and hydrogen,  $R_{33}$  is selected from the group consisting of hydrogen, a monovalent hydrocarbon having from 1 to 10 carbon atoms and



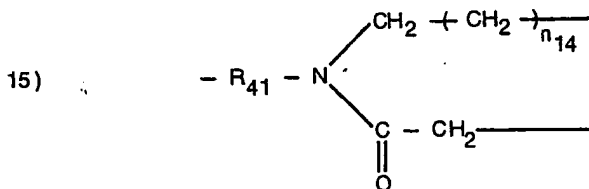
wherein  $R_{34}$  is a monovalent hydrocarbon having from 1 to 10 carbon atoms and  $n_{12}$  is at least 1,



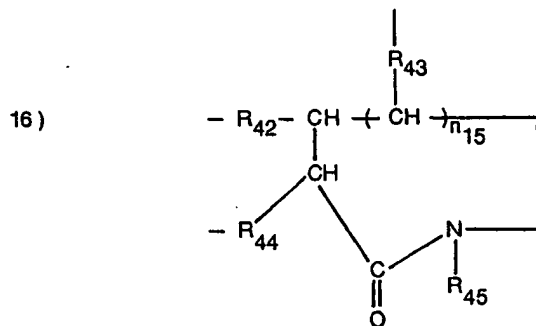
25 wherein  $R_{35}$  is a divalent hydrocarbon having from 1 to 10 carbon atoms,  $R_{36}$  and  $R_{37}$  can be the same or different and are selected from the group consisting of hydrogen, monovalent hydrocarbons having from 1 to 10 carbon atoms and  $-(\text{CH}_2)_{n_{13}}-\text{OH}$  wherein  $n_{13}$  is 2 to 4,



35 wherein  $R_{38}$  is a divalent hydrocarbon having from 1 to 10 carbon atoms and the S atom cannot be attached to a carbon atom of  $R_{38}$  which is alpha to the Si atom,  $R_{39}$  and  $R_{40}$  can be the same or different and are selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 10 carbon atoms,

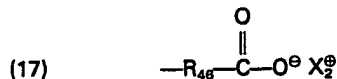


wherein  $R_{41}$  is a divalent hydrocarbon having from 1 to 10 carbon atoms and  $n_{14}$  is an integer from zero to 3,

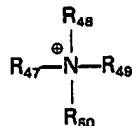


55 wherein  $n_{15}$  is an integer from zero to 3,  $R_{42}$  and  $R_{43}$  are selected from the group consisting of hydrogen, divalent or monovalent hydrocarbon having from 0 to 10 carbon atoms and  $R_{44}$  is selected from the group  
65 consisting of hydrogen, divalent or monovalent hydrocarbon having from 1 to 10 carbon atoms and only

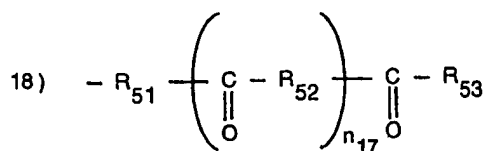
one of  $R_{42}$ ,  $R_{43}$  and  $R_{44}$  must be a divalent hydrocarbon and attached to the Si atom,  $R_{45}$  is selected from the group consisting of hydrogen, a monovalent hydrocarbon having from 1 to 10 carbon atoms and  $-(CH_2)_{n_{16}}-OH$  wherein  $n_{16}$  is an integer from 2 to 4,



wherein  $R_{46}$  is a divalent hydrocarbon having from 2 to 10 carbon atoms and the carbonyl group cannot be attached to a carbon atom alpha to the Si atom and  $X_2^{\oplus}$  is a monovalent cation selected from the group consisting of monovalent metal cations and



wherein  $R_{47}$ ,  $R_{48}$ ,  $R_{49}$  and  $R_{50}$  are the same or different and are selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 10 carbon atoms,

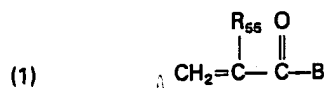


wherein  $R_{51}$  is a divalent hydrocarbon having from 1 to 10 carbon atoms and the carbonyl group cannot be attached to a carbon atom which is alpha to the Si atom,  $R_{52}$  is a divalent hydrocarbon having from one to 10 carbon atoms,  $R_{53}$  is selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 10 carbon atoms and  $n_{17}$  is an integer from zero to 10, and



wherein  $R_{54}$  is a hydrocarbon having from 1 to 20 carbon atoms and having a valence of  $n_{18} + 1$  and no  $-C \equiv N$  group is attached to a carbon atom of  $R_{54}$  which is alpha to the Si atom and  $n_{18}$  is an integer greater than zero;

(B) polymerized with a comonomer selected from the group consisting of



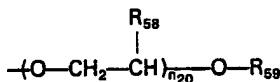
wherein  $R_{55}$  is selected from the group of hydrogen and methyl and B is selected from the group consisting of



wherein  $R_{56}$  is selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 20 carbon atoms,



wherein  $R_{57}$  is a hydrocarbon having from 2 to 20 carbon atoms and a valence of  $n_{19} + 1$  and can have no more than one oxygen atom attached to any one carbon atom and  $n_{19}$  is an integer greater than zero,



wherein  $R_{58}$  is selected from the group consisting of hydrogen and methyl,  $R_{59}$  is selected from the group consisting of hydrogen, a monovalent hydrocarbon having from 1 to 20 carbon atoms,



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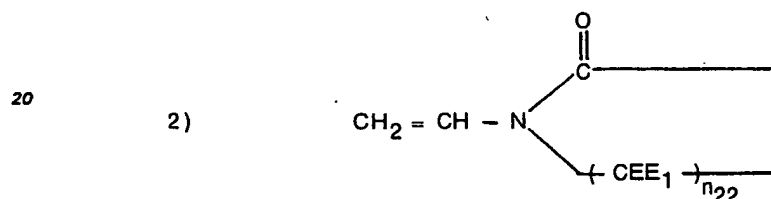
wherein  $R_{60}$  is a monovalent hydrocarbon having from 1 to 20 carbon atoms and  $n_{20}$  is an integer greater than zero,



wherein  $R_{61}$  and  $R_{62}$  are the same or different and are selected from the group consisting of hydrogen, a monovalent hydrocarbon having from 1 to 20 carbon atoms and  $\text{---(CH}_2\text{)}_{n_{21}}\text{---D}$  wherein D is selected from the group consisting of  $\text{---OH}$  and



wherein  $R_{63}$  and  $R_{64}$  are the same or different and are hydrogens and monovalent hydrocarbons having from 1 to 20 carbon atoms and  $n_{21}$  is an integer from 2 to 3,



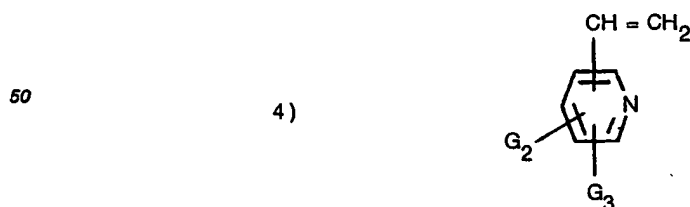
wherein E and  $E_1$  are the same or different and are selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 10 carbon atoms and  $n_{22}$  is an integer from 2 to 5,



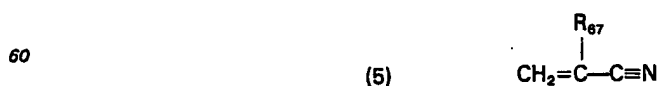
wherein G and  $G_1$  are the same or different and are selected from the group consisting of hydrogen, a halogen, a monovalent hydrocarbon having from 1 to 20 carbon atoms, hydroxyl,



wherein  $R_{65}$  and  $R_{66}$  are the same or different and are selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 20 carbon atoms,

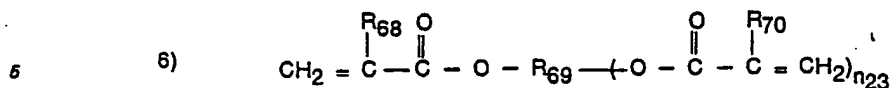


wherein  $G_2$  and  $G_3$  are the same or different and are selected from the group consisting of hydrogen and a monovalent hydrocarbon having from 1 to 10 carbon atoms,

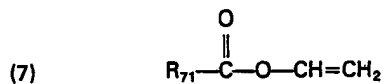


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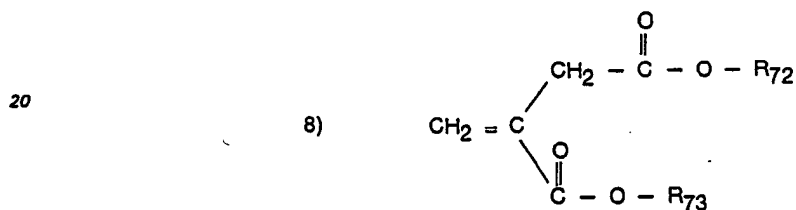
wherein  $R_{67}$  is selected from the group consisting of hydrogen and methyl,



wherein  $R_{68}$  and  $R_{70}$  are the same or different and are selected from the group consisting of hydrogen and methyl,  $R_{69}$  is a hydrocarbon having from 1 to 20 carbon atoms and a valence of  $n_{23} + 1$  and  $n_{23}$  is an integer from 1 to 5,



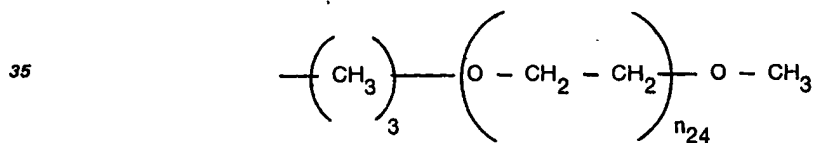
wherein  $R_{71}$  is a monovalent hydrocarbon having from 1 to 20 carbon atoms and



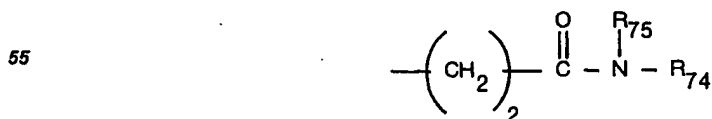
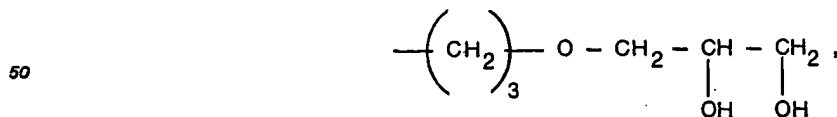
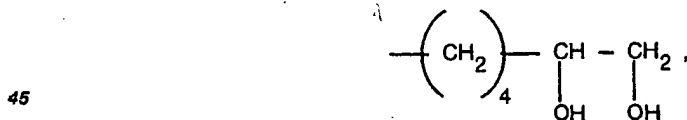
wherein  $R_{72}$  and  $R_{73}$  are the same or different and are selected from the group consisting of hydrogen and monovalent hydrocarbon having from 1 to 20 carbon atoms,

(C) forming a polymer in a crosslinked network capable upon saturation with water of retaining from about 1 percent to about 99 percent by weight of water, based on the total weight of the polymer and water.

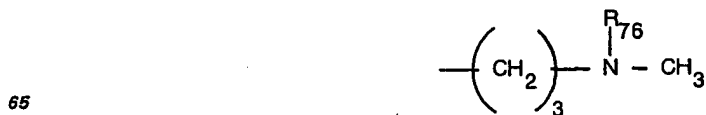
2. An article according to Claim 1 wherein said hydrophilic sidechain is selected from the group consisting of



wherein  $n_{24}$  is an integer from 2 to 3,

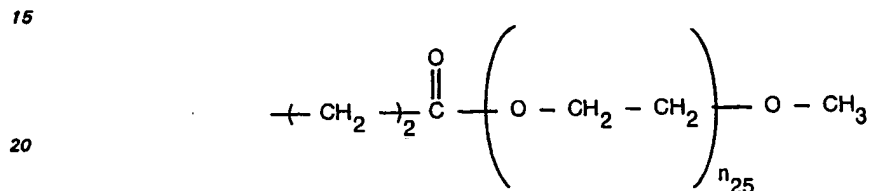
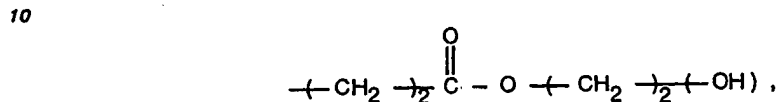


wherein  $R_{74}$  and  $R_{75}$  are the same or different and are selected from the group consisting of hydrogen, methyl and  $-\text{CH}_2-\text{CH}_2-\text{OH}$ ,

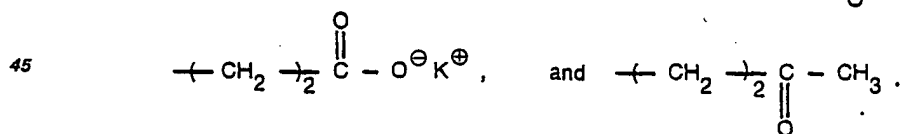
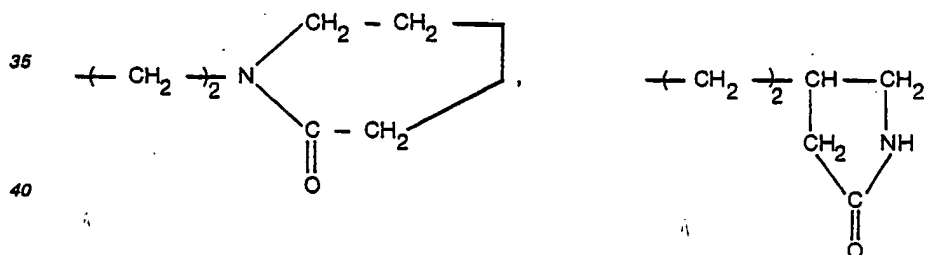
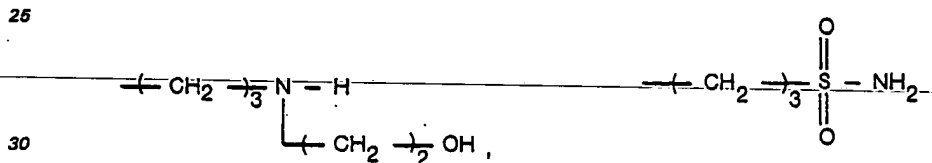


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wherein  $R_{76}$  is selected from the group consisting of hydrogen and methyl,



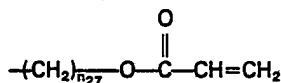
wherein  $n_{25}$  is an integer from 2 to 3



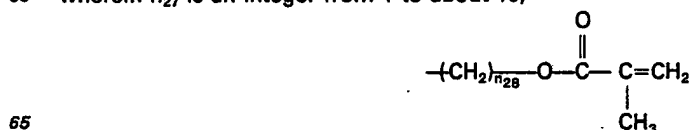
**3. An article according to Claim 1 or Claim 2, wherein X is selected from the group consisting of**



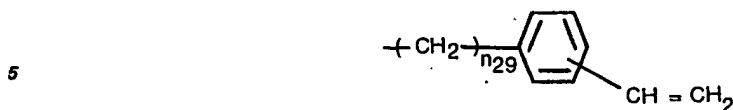
55 wherein  $n_{26}$  is an integer from 1 to about 10,



60 wherein  $n_{27}$  is an integer from 1 to about 10,

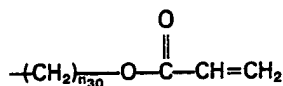


wherein  $n_{28}$  is an integer from 1 to about 10 and

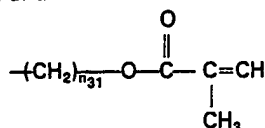


wherein  $n_{29}$  is an integer from 0 to about 10.

10 4. An article according to Claim 3 wherein X is selected from the group consisting of



15 wherein  $n_{30}$  is an integer from 3 to 4, and

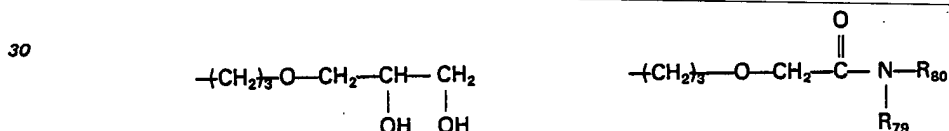


20 wherein  $n_{31}$  is an integer from 3 to 4.

5. An article according to any preceding claim, wherein only one of  $Z_1$ ,  $Z_2$ ,  $Z_5$  and  $Z_6$  is a hydrophilic side chain.

6. An article according to Claim 5 wherein a is equal to about 10 to about 500, b is equal to zero, c is equal to 1, d is equal to about 10 to about 500, e is equal to 1 and f is equal to zero.

25 7. An article according to Claim 6 wherein  $Z_1$ ,  $Z_2$  and  $Z_5$  are methyls and  $Z_6$  is selected from the group consisting of  $\text{-(CH}_2\text{)}_3\text{-(O-CH}_2\text{-CH}_2\text{)}_{n_{33}}\text{-O-CH}_3$  wherein  $n_{33}$  is an integer from 2 to 3,



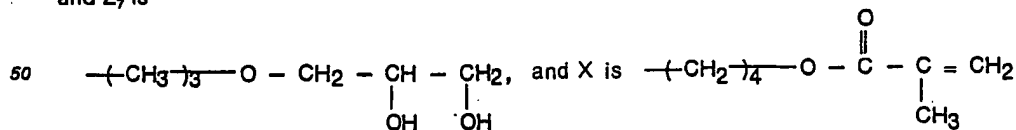
35 wherein  $R_{79}$  is selected from the group consisting of methyl and hydrogen,  $R_{80}$  is selected from the group consisting of methyl, hydrogen and  $\text{-CH}_2\text{-CH}_2\text{-OH}$ ,  $Y_1$  and  $Y_2$  equal methyl and X equals



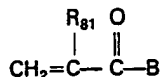
wherein  $n_{34}$  is an integer from 3 to 4.

45 8. An article according to any one of Claims 1—4 wherein only one of  $Z_1$ — $Z_7$  is a hydrophilic side chain.

9. An article according to Claim 8 wherein  $Z_1$ ,  $Z_2$ ,  $Z_5$ ,  $Z_6$ ,  $Y_1$  and  $Y_2$  are methyls,  $Z_3$  and  $Z_4$  are hydrogens and  $Z_7$  is

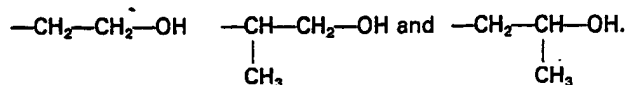


55 10. An article according to any preceding claim wherein the comonomer is

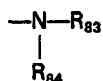


60 wherein  $R_{81}$  is selected from the group consisting of hydrogen and methyl and B is  $\text{-O-R}_{82}$  wherein  $R_{82}$  is selected from the group consisting of a monovalent hydrocarbon having from 1 to 12 carbon atoms, a monovalent hydrocarbon derivative having from 1 to 12 carbon atoms and hydrogen.

11. An article according to Claim 10 wherein  $R_{82}$  is selected from the group consisting of

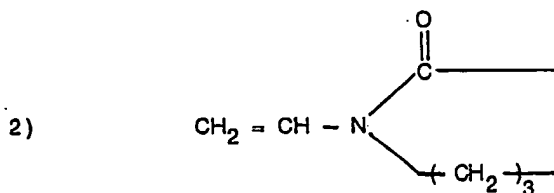


12. An article according to Claim 10 or Claim 11 wherein B is



wherein  $R_{83}$  and  $R_{84}$  are the same or different and are selected from the group consisting of hydrogen, methyl and  $\text{---CH}_2\text{---CH}_2\text{---OH}$ .

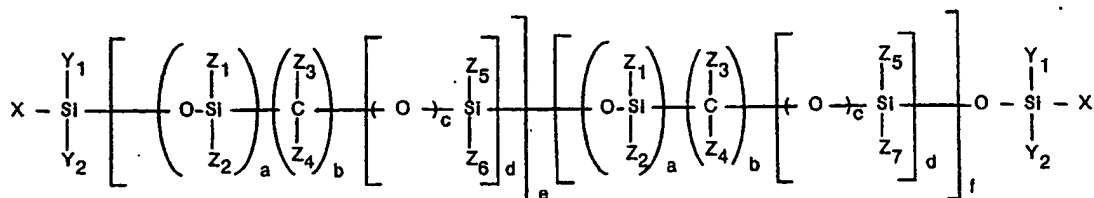
13. An article according to any one of Claims 1—9 wherein the comonomer is



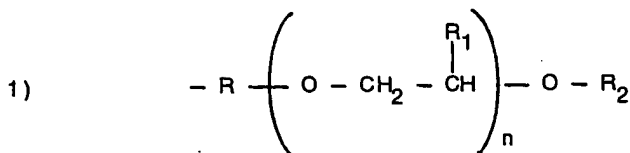
14. An article according to any preceding claim, being a water absorbing, soft, hydrophilic, flexible, hydrolytically stable, biologically inert contact lens with the capability of transporting oxygen sufficiently to meet the requirements of the human cornea.

# Patentansprüche

1. Zur Verwendung in biomedizinischen Anwendungen geeigneter geformter Gegenstand hergestellt aus einem Polymer, das gekennzeichnet ist durch:  
(A) ein Polysiloxanmonomer mit der folgenden Formel:



in der  $Y_1$  und  $Y_2$  gleich oder verschieden sind und ausgewählt sind aus der Gruppe bestehend aus Kohlenwasserstoffen mit 1 bis 20 Kohlenstoffatomen und halogenierten Kohlenwasserstoffen mit 1 bis 20 Kohlenstoffatomen, X eine durch eine zweiwertige Kohlenwasserstoffgruppe gebundene, aktivierte ungesättigte Gruppe ist, a mindestens 1 ist, b 0 oder mindestens 2 ist, c 1 ist, wenn b 0 ist, und c 0 ist, wenn b mindestens 2 ist, d mindestens 1 ist, ausgenommen wenn b 0 ist und a 1 ist, dann ist d 0 oder größer, e mindestens 1 ist und f 0 oder größer ist,  $Z_1$  bis  $Z_7$  gleich oder verschieden sind, mindestens eine der  $Z_1$ — $Z_7$ -Gruppen eine hydrophile Seitenkette ist und  $Z_1$  bis  $Z_7$  ausgewählt sind aus der Gruppe bestehend aus einem einwertigen Kohlenwasserstoff mit 1 bis 20 Kohlenstoffatomen, einem halogenierten einwertigen Kohlenwasserstoff mit 1 bis 20 Kohlenstoffatomen und einer hydrophilen Seitenkette mit den folgenden Formeln ausgewählt aus der Gruppe bestehend aus



w bei R ein zweiwertiger Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen ist,  $R_1$  ausgewählt ist aus der



Gruppe bestehend aus Methyl und Wasserstoff,  $R_2$  ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, einem einwertigen Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen und

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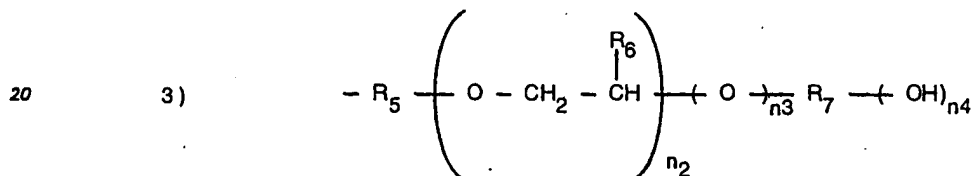
mit  $R_3$  ausgewählt aus der Gruppe bestehend aus einem einwertigen Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen und Wasserstoff und  $n$  mindestens 1 ist,

10



wobei  $R_4$  ein Kohlenwasserstoff mit 1 bis 20 Kohlenstoffatomen und einer Wertigkeit von  $n_1 + 1$  ist, wobei  $n_1$  mindestens 1 ist und sich keine OH-Gruppe an einem aliphatischen Kohlenstoffatom in  $\beta$ -Stellung zum Si-Atom befinden darf und sich an keinem Kohlenstoffatomen mehr als ein Sauerstoffatom befinden kann,

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25

wobei  $R_5$  ein zweiwertiger Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen ist,  $R_6$  ausgewählt ist aus der Gruppe bestehend aus Wasserstoff und Methyl und  $R_7$  ein Kohlenwasserstoff mit 1 bis 20 Kohlenstoffatomen und einer Wertigkeit von  $n_4 + 1$  ist und nicht mehr als ein Sauerstoffatom an jedes Kohlenstoffatom gebunden haben darf,  $n_2$  0 oder größer ist,  $n_3$  eine ganze Zahl von 0 bis 1 ist und  $n_4$  mindestens 1 ist,

30



wobei  $R_8$  ein zweiwertiger Kohlenwasserstoff mit 2 bis 10 Kohlenstoffatomen ist und die

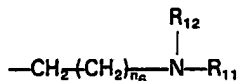
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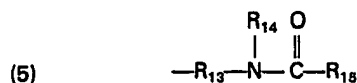
Gruppe nicht an ein Kohlenstoffatom von  $R_8$  gebunden ist, das sich in  $\alpha$ -Stellung zum Si-Atom befindet,  $R_9$  und  $R_{10}$  gleich oder verschieden sein können und ausgewählt sind aus der Gruppe bestehend aus einem einwertigen Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen, Wasserstoff,  $-\text{CH}_2-(\text{CH}_2)_{n_5}-\text{OH}$ , wobei  $n_5$  eine ganze Zahl von 1 bis 3 ist, und

45



wobei  $R_{11}$  und  $R_{12}$  gleich oder verschieden sind und ausgewählt sind aus der Gruppe bestehend aus Wasserstoff und einem einwertigen Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen und  $n_6$  eine ganze Zahl von 1 bis 5 ist,

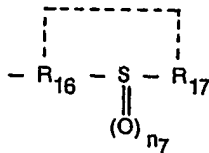
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wobei  $R_{13}$  ein zweiwertiger Kohlenwasserstoff mit 1 bis 20 Kohlenstoffatomen ist und  $R_{14}$  und  $R_{15}$  gleich oder verschieden sind und ausgewählt sind aus der Gruppe bestehend aus Wasserstoff und einem einwertigen Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen,

60

6)

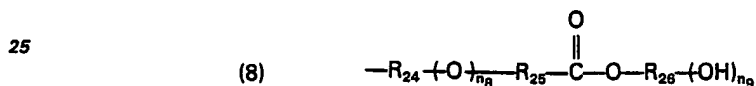


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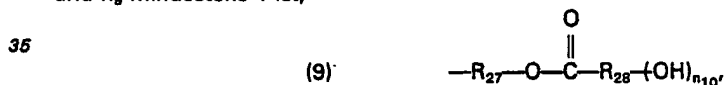
wobei  $R_{18}$  ein zweiwertiger oder dreiwertiger Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen ist und das S-Atom nicht an  $R_{18}$  durch ein aliphatisches Kohlenstoffatom gebunden ist, das sich in  $\beta$ -Stellung zum Si-Atom befindet,  $R_{16}$  an  $R_{17}$  unter Bildung eines Rings mit mehr als 3 Kohlenstoffatomen gebunden sein kann oder nicht und  $R_{17}$  ausgewählt ist aus der Gruppe bestehend aus einem Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen und  $-O^{\ominus} M^{\oplus}$ , wobei  $M$  ausgewählt ist aus der Gruppe bestehend aus einem einwertigen Metallion und einem quaternären Ammoniumion, und  $n_7$  eine ganze Zahl von 1 bis 2 ist,



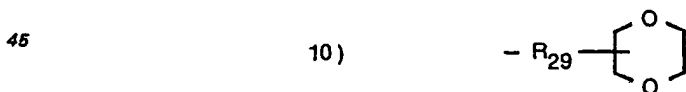
15 wobei  $R_{18}$  ein zweiwertiger Kohlenwasserstoff mit 3 bis 10 Kohlenstoffatomen ist und  $N^{\oplus}$  an ein Kohlenstoffatom von  $R_{18}$  gebunden sein muß, das mindestens zwei Kohlenstoffatome vom Si-Atom entfernt ist,  $R_{19}$ ,  $R_{20}$  und  $R_{21}$  gleich oder verschieden sind und einwertige Kohlenwasserstoffe mit 1 bis 10 Kohlenstoffatomen sind,  $X_1^{\ominus}$  ein einwertiges Anion ausgewählt aus der Gruppe bestehend aus Halogeniden,  $R_{22}-COO^{\ominus}$ , wobei  $R_{22}$  ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, einem einwertigen Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen und einem halogenierten einwertigen Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen, und  $R_{23}-SO_3^{\ominus}$ , wobei  $R_{23}$  ausgewählt ist aus der Gruppe bestehend aus einem einwertigen Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen und einem halogenierten einwertigen Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen



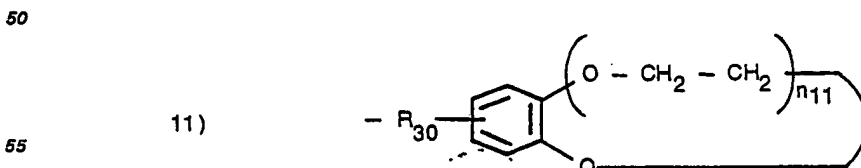
30 wobei  $R_{24}$  ein zweiwertiger Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen ist und  $n_8$  eine ganze Zahl von 0 bis 1 ist und der Sauerstoff nicht an ein aliphatisches Kohlenstoffatom in  $R_{24}$ , das sich in  $\beta$ -Stellung zum Si-Atom befindet, gebunden sein kann, wenn  $n_8$  1 ist,  $R_{25}$  ein zweiwertiger Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen ist,  $R_{26}$  ein Kohlenwasserstoff mit 2 bis 20 Kohlenstoffatomen und einer Wertigkeit von  $n_9 + 1$  ist und nicht mehr als ein Sauerstoffatom an jedes Kohlenstoffatom gebunden haben kann, und  $n_9$  mindestens 1 ist,



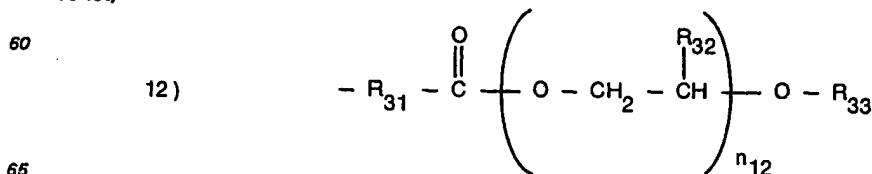
40 wobei  $R_{27}$  ein zweiwertiger Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen ist und das an  $R_{27}$  gebundene Sauerstoffatom nicht an ein aliphatisches Kohlenstoffatom in  $R_{27}$  gebunden sein kann, das sich in  $\beta$ -Stellung zum Si-Atom befindet,  $R_{28}$  ein Kohlenwasserstoff mit 1 bis 20 Kohlenstoffatomen und einer Wertigkeit von  $n_{10} + 1$  ist und nicht mehr als 1 Sauerstoffatom an jedes Kohlenstoffatom gebunden haben kann, und  $n_{10}$  eine ganze Zahl von mindestens 1 ist,



wobei  $R_{29}$  ein zweiwertiger Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen ist,

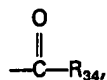


55 wobei  $R_{30}$  ein zweiwertiger Kohlenstoff mit 0 bis 10 Kohlenstoffatomen ist und  $n_{11}$  eine ganze Zahl von 1 bis 10 ist,

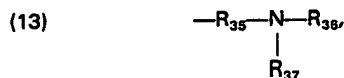


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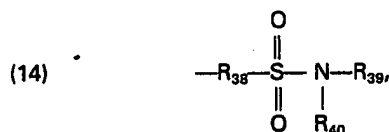
wobei  $R_{31}$  ein zweiwertiger Kohlenwasserstoff mit 2 bis 10 Kohlenstoffatomen ist und die Carbonylgruppe nicht an ein Kohlenstoffatom in alpha-Stellung zum Si-Atom gebunden ist,  $R_{32}$  ausgewählt ist aus der Gruppe bestehend aus Methyl und Wasserstoff,  $R_{33}$  ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, einem einwertigen Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen und



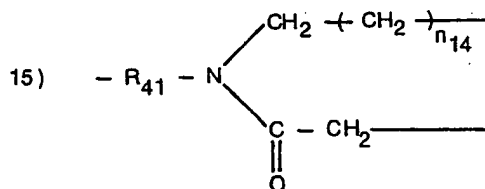
wobei  $R_{34}$  ein einwertiger Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen ist, und  $n_{12}$  mindestens 1 ist,



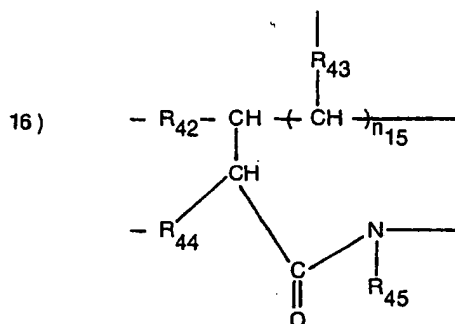
wobei  $R_{35}$  ein zweiwertiger Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen ist,  $R_{36}$  und  $R_{37}$  gleich oder verschieden sein können und ausgewählt sind aus der Gruppe bestehend aus Wasserstoff, einwertigen Kohlenwasserstoffen mit 1 bis 10 Kohlenstoffatomen und  $-(\text{CH}_2)_{n_{13}}-\text{OH}$ , wobei  $n_{13}$  2 bis 4 ist,



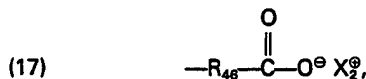
wobei  $R_{38}$  ein zweiwertiger Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen ist und das S-Atom nicht an ein Kohlenstoffatom von  $R_{38}$  gebunden sein kann, das sich in alpha-Stellung zum Si-Atom befindet,  $R_{39}$  und  $R_{40}$  gleich oder verschieden sein können und ausgewählt sind aus der Gruppe bestehend aus Wasserstoff und einem einwertigen Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen,



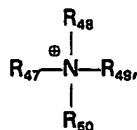
wobei  $R_{41}$  ein zweiwertiger Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen ist und  $n_{14}$  eine ganze Zahl von 0 bis 3 ist,



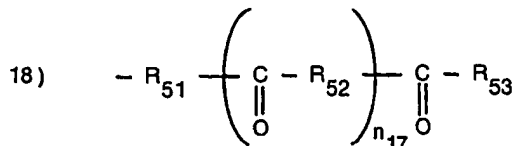
wobei  $n_{15}$  eine ganze Zahl von 0 bis 3 ist,  $R_{42}$  und  $R_{43}$  ausgewählt sind aus der Gruppe bestehend aus Wasserstoff, zweiwertigem oder einwertigem Kohlenwasserstoff mit 0 bis 10 Kohlenstoffatomen,  $R_{44}$  ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, zweiwertigem oder einwertigem Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen, nur einer von  $R_{42}$ ,  $R_{43}$  und  $R_{44}$  ein zweiwertiger Kohlenwasserstoff und an das Si-Atom gebunden sein muß,  $R_{45}$  ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, einem einwertigen Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen und  $-(\text{CH}_2)_{n_{16}}-\text{OH}$ , wobei  $n_{16}$  eine ganze Zahl von 2 bis 4 ist,



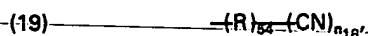
wobei  $R_{46}$  ein zweiwertiger Kohlenwasserstoff mit 2 bis 10 Kohlenstoffatomen ist und die Carbonylgruppe nicht an ein Kohlenstoffatom in alpha-Stellung zum Si-Atom gebunden sein kann und  $X_2$  ein einwertiges Kation ausgewählt aus der Gruppe bestehend aus einwertigen Metallkationen und



wobei  $R_{47}$ ,  $R_{48}$ ,  $R_{49}$  und  $R_{50}$  gleich oder verschieden sind und ausgewählt sind aus der Gruppe bestehend aus Wasserstoff und einem einwertigen Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen,



wobei  $R_{51}$  ein zweiwertiger Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen ist und die Carbonylgruppe nicht an ein Kohlenstoffatom gebunden sein kann, das sich in alpha-Stellung zum Si-Atom befindet,  $R_{52}$  ein zweiwertiger Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen ist,  $R_{53}$  ausgewählt ist aus der Gruppe bestehend aus Wasserstoff und einem einwertigen Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen und  $n_{17}$  eine ganze Zahl von 0 bis 10 ist, und



wobei  $R_{54}$  ein Kohlenwasserstoff mit 1 bis 20 Kohlenstoffatomen ist und eine Wertigkeit von  $n_{18} + 1$  besitzt und keine  $-C \equiv N$ -Gruppe an ein Kohlenstoffatom von  $R_{54}$  gebunden ist, das sich in alpha-Stellung zum Si-Atom befindet, und  $n_{18}$  eine ganze Zahl ist, die größer als 0 ist;

(B) Polymerisation mit einem Comonomer ausgewählt aus der Gruppe bestehend aus



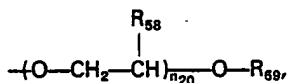
wobei  $R_{55}$  ausgewählt ist aus der Gruppe aus Wasserstoff und Methyl und B ausgewählt ist aus der Gruppe bestehend aus



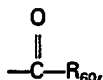
wobei  $R_{56}$  ausgewählt ist aus der Gruppe bestehend aus Wasserstoff und einem einwertigen Kohlenwasserstoff mit 1 bis 20 Kohlenstoffatomen,



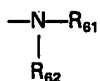
wobei  $R_{57}$  ein Kohlenwasserstoff mit 2 bis 20 Kohlenstoffatomen und einer Wertigkeit von  $n_{19} + 1$  ist und nicht mehr als 1 Sauerstoffatom an jedes Kohlenstoffatom gebunden haben kann und  $n_{19}$  eine ganze Zahl von mehr als 0 ist,



wobei  $R_{58}$  ausgewählt ist aus der Gruppe bestehend aus Wasserstoff und Methyl,  $R_{59}$  ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, einem einwertigen Kohlenwasserstoff mit 1 bis 20 Kohlenstoffatomen und



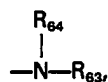
wobei  $R_{60}$  ein einwertiger Kohlenwasserstoff mit 1 bis 20 Kohlenstoffatomen ist und  $n_{20}$  eine ganze Zahl von mehr als 0 ist, und



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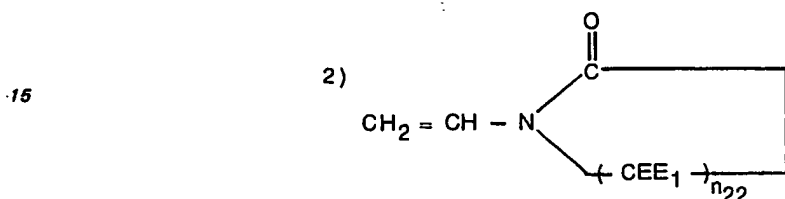
wobei  $R_{61}$  und  $R_{62}$  gleich oder verschieden sind und ausgewählt sind aus der Gruppe bestehend aus Wasserstoff, einem einwertigen Kohlenwasserstoff mit 1 bis 20 Kohlenstoffatomen und  $-(CH_2)_{n_2}D$ , wobei D ausgewählt ist aus der Gruppe bestehend aus  $-OH$  und

5



wobei  $R_{63}$  und  $R_{64}$  gleich oder verschieden sind und Wasserstoffe und einwertige Kohlenwasserstoffe mit 1 bis 20 Kohlenstoffatomen sind, und  $n_{21}$  eine ganze Zahl von 2 bis 3 ist,

10

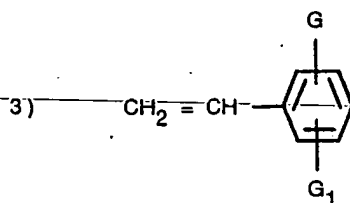


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wobei E und  $E_1$  gleich oder verschieden sind und ausgewählt sind aus der Gruppe bestehend aus Wasserstoff und einem einwertigen Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen und  $n_{22}$  eine ganze Zahl von 2 bis 5 ist,

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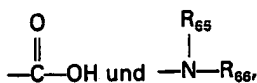
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wobei G und  $G_1$  gleich oder verschieden sind und ausgewählt sind aus der Gruppe bestehend aus Wasserstoff, einem Halogen, einem einwertigen Kohlenwasserstoff mit 1 bis 20 Kohlenstoffatomen, einer Hydroxylgruppe,

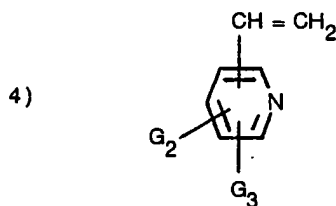
35



wobei  $R_{65}$  und  $R_{66}$  gleich oder verschieden sind und ausgewählt sind aus der Gruppe bestehend aus Wasserstoff und einem einwertigen Kohlenwasserstoff mit 1 bis 20 Kohlenstoffatomen,

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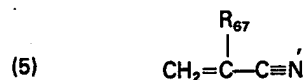
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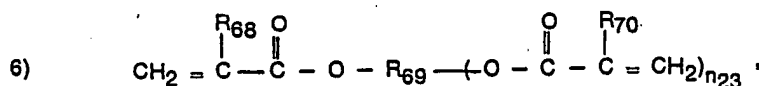
wobei  $G_2$  und  $G_3$  gleich oder verschieden sind und ausgewählt sind aus der Gruppe bestehend aus Wasserstoff und einem einwertigen Kohlenwasserstoff mit 1 bis 10 Kohlenstoffatomen,

55



wobei  $R_{67}$  ausgewählt ist aus der Gruppe bestehend aus Wasserstoff und Methyl,

60



wobei  $R_{68}$  und  $R_{70}$  gleich oder verschieden sind und ausgewählt sind aus der Gruppe bestehend aus

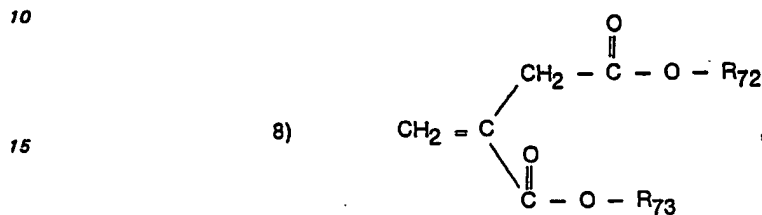
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Wasserstoff und Methyl,  $R_{69}$  ein Kohlenwasserstoff mit 1 bis 20 Kohlenstoffatomen und einer Wertigkeit von  $n_{23} + 1$  ist und  $n_{23}$  eine ganze Zahl von 1 bis 5 ist,



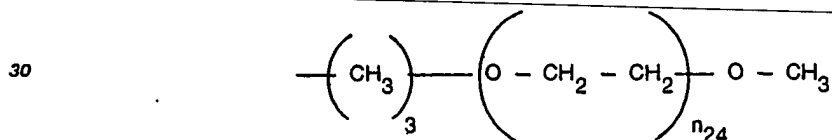
wobei  $R_{71}$  ein einwertiger Kohlenwasserstoff mit 1 bis 20 Kohlenstoffatomen ist, und



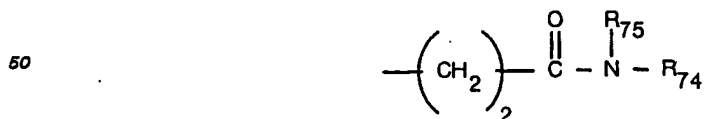
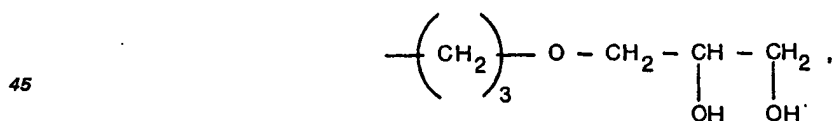
wobei  $R_{72}$  und  $R_{73}$  gleich oder verschieden sind und ausgewählt sind aus der Gruppe bestehend aus Wasserstoff und einwertigem Kohlenwasserstoff mit 1 bis 20 Kohlenstoffatomen, und

(C) Bildung eines Polymeren in Form eines vernetzten Netzwerkes, welches bei Sättigung mit Wasser etwa 1 bis 99 Gew.% Wasser, bezogen auf das Gesamtgewicht aus Polymer und Wasser, zurückhalten kann.

2. Gegenstand nach Anspruch 1, dadurch gekennzeichnet, daß die hydrophile Seitenkette ausgewählt ist aus der Gruppe bestehend aus



wobei  $n_{24}$  eine ganze Zahl von 2 bis 3 ist,

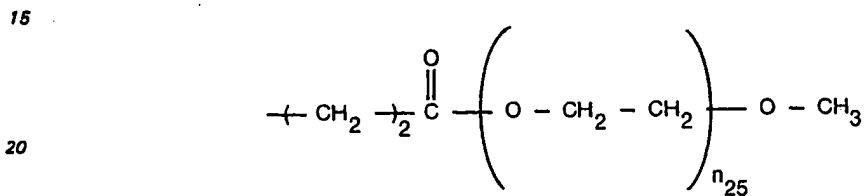
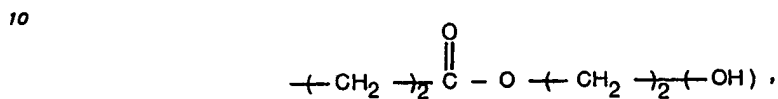


wobei  $R_{74}$  und  $R_{75}$  gleich oder verschieden sind und ausgewählt sind aus der Gruppe bestehend aus Wasserstoff, Methyl und  $-\text{CH}_2-\text{CH}_2-\text{OH}$ ,

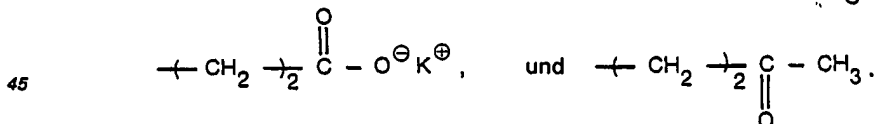
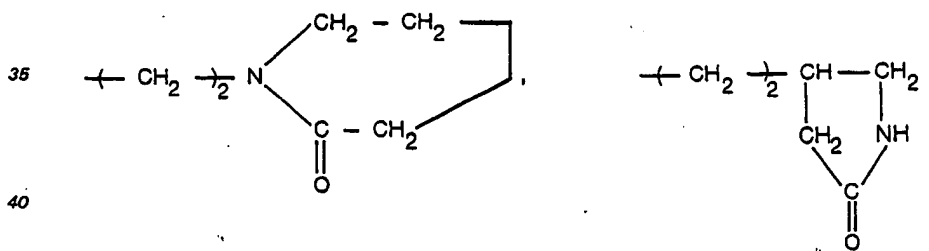
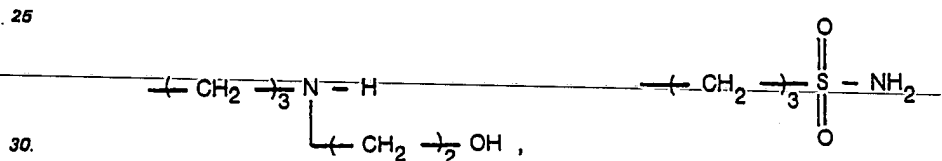


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wobei  $R_{76}$  ausgewählt ist aus der Gruppe bestehend aus Wasserstoff und Methyl,



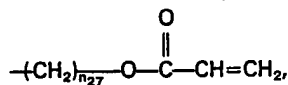
wobei  $n_{25}$  eine ganze Zahl von 2 bis 3 ist,



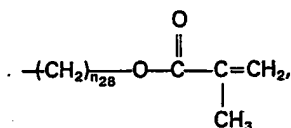
3. Gegenstand nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß X ausgewählt ist aus der Gruppe bestehend aus



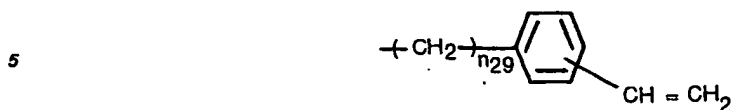
wobei  $n_{26}$  eine ganze Zahl von 1 bis etwa 10 ist,



wobei  $n_{27}$  eine ganze Zahl von 1 bis etwa 10 ist,

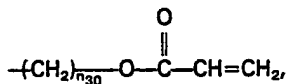


wobei  $n_{28}$  eine ganze Zahl von 1 bis etwa 10 ist, und

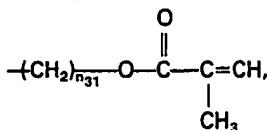


wobei  $n_{29}$  eine ganze Zahl von 0 bis etwa 10 ist.

4. Gegenstand nach Anspruch 3, dadurch gekennzeichnet, daß X ausgewählt ist aus der Gruppe bestehend aus



15 wobei  $n_{30}$  eine ganze Zahl von 3 bis 4 ist, und

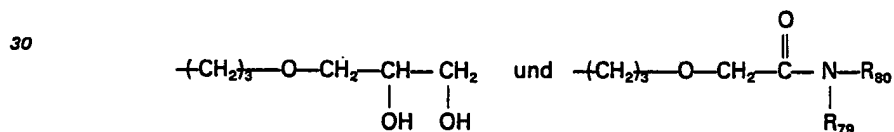


20 wobei  $n_{31}$  eine ganze Zahl von 3 bis 4 ist.

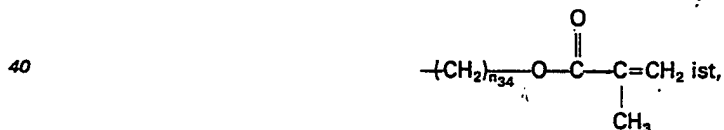
5. Gegenstand nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß nur eine der Gruppen  $Z_1$ ,  $Z_2$ ,  $Z_5$  und  $Z_6$  eine hydrophile Seitenkette ist.

6. Gegenstand nach Anspruch 5, dadurch gekennzeichnet, daß a gleich etwa 10 bis etwa 500 ist, b gleich 0 ist, c gleich 1 ist, d gleich etwa 10 bis etwa 500 ist, e gleich 1 ist und f gleich 0 ist.

7. Gegenstand nach Anspruch 6, dadurch gekennzeichnet, daß  $Z_1$ ,  $Z_2$  und  $Z_6$  Methylreste sind und  $Z_5$  ausgewählt ist aus der Gruppe bestehend aus  $\text{-(CH}_2\text{)}_{n_{33}}\text{-(O-CH}_2\text{-CH}_2\text{)}_{n_{33}}\text{-O-CH}_3$ , wobei  $n_{33}$  eine ganze Zahl von 2 bis 3 ist



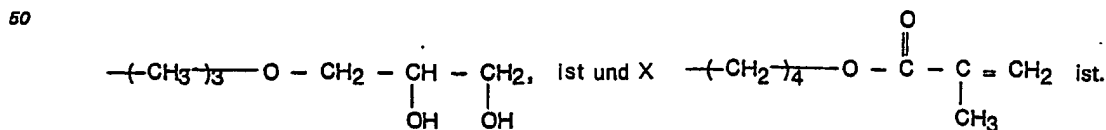
35 wobei  $R_{79}$  ausgewählt ist aus der Gruppe bestehend aus Methyl und Wasserstoff und  $R_{80}$  ausgewählt ist aus der Gruppe bestehend aus Methyl, Wasserstoff und  $\text{-CH}_2\text{-CH}_2\text{-OH}$ ,  $Y_1$  und  $Y_2$  Methylgruppen sind und X



wobei  $n_{34}$  eine ganze Zahl von 3 bis 4 ist.

45 8. Gegenstand nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß nur eine der Gruppen  $Z_1$ — $Z_7$  eine hydrophile Seitenkette ist.

9. Gegenstand nach Anspruch 8, dadurch gekennzeichnet, daß  $Z_1$ ,  $Z_2$ ,  $Z_3$ ,  $Z_6$ ,  $Y_1$  und  $Y_2$  Methylreste sind,  $Z_3$  und  $Z_4$  Wasserstoffe sind und  $Z_7$



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10. Gegenstand nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß das Comonomer

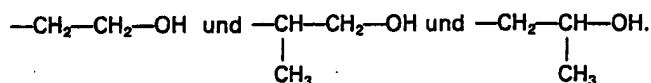


ist, wobei  $R_{81}$  ausgewählt ist aus der Gruppe bestehend aus Wasserstoff und Methyl und  $\text{B-O-R}_{82}$  ist, wobei  $R_{82}$  ausgewählt ist aus der Gruppe bestehend aus einem einwertigen Kohlenwasserstoff mit 1 bis 12 Kohlenstoffatomen, einem einwertigen Kohlenwasserstoffderivat mit 1 bis 12 Kohlenstoffatomen und Wasserstoff.

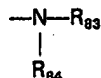
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11. Gegenstand nach Anspruch 10, dadurch gekennzeichnet, daß  $R_{82}$  ausg gewählt ist aus der Gruppe bestehend aus

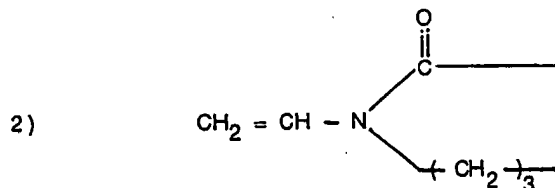


12. Gegenstand nach Anspruch 10 oder 11, dadurch gekennzeichnet, daß B



ist, wobei  $R_{83}$  und  $R_{84}$  gleich oder verschieden sind und ausgewählt sind aus der Gruppe bestehend aus Wasserstoff, Methyl und  $\text{—CH}_2\text{—CH}_2\text{—OH}$ .

13. Gegenstand nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß das Comonomer



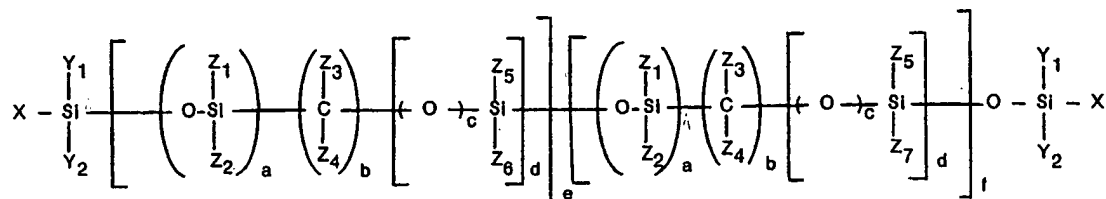
ist.

14. Gegenstand nach einem der vorangehenden Ansprüche, bei dem es sich um eine Wasser absorbierende, weiche, hydrophile, flexible, hydrolytisch stabile, biologisch inerte Kontaktlinse mit der Fähigkeit eines ausreichenden-Sauerstofftransports-zur-Erfüllung der Erfordernisse der Hornhaut des menschlichen Auges handelt.

#### Revendications

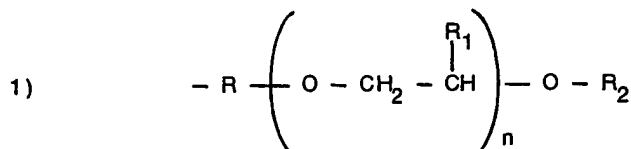
1. Object façonné pouvant être utilisé pour des applications biomédicales et formé à partir d'un polymère comportant:

A) un polysiloxane monomère ayant la formule suivante:



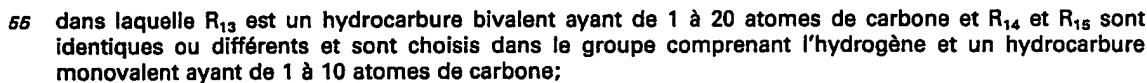
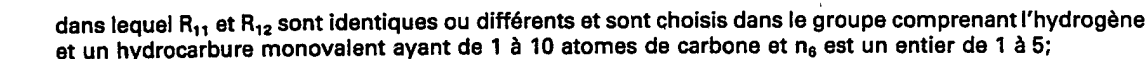
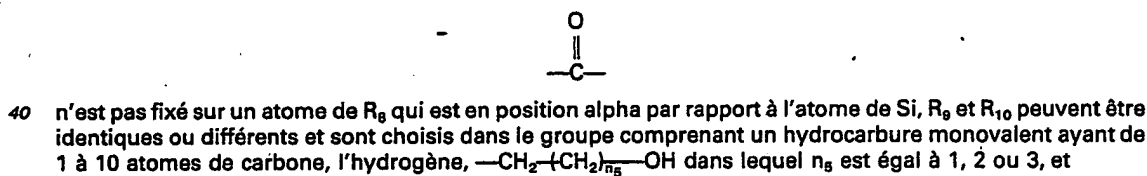
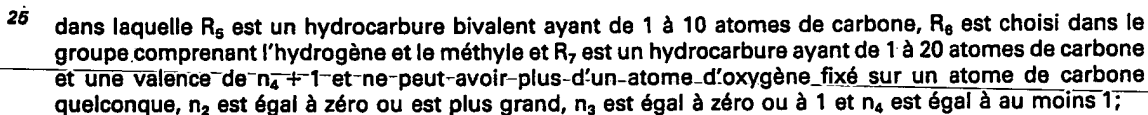
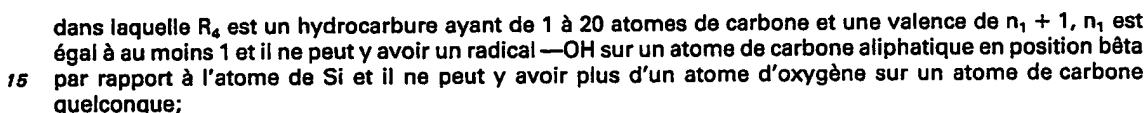
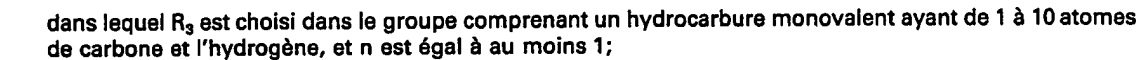
dans laquelle  $Y_1$  et  $Y_2$  sont identiques ou différents et sont choisis dans le groupe comprenant un hydrocarbure ayant de 1 à 20 atomes de carbone et un hydrocarbure halogéné ayant de 1 à 20 atomes de carbone, X est un radical non saturé activé lié par un radical hydrocarboné bivalent, a est au moins égal à 1, b est égal à zéro ou à au moins 2, c est égal à 1 si b est égal à zéro et c est égal à zéro si b est égal à au moins 2, d est égal à au moins 1, sauf si b est égal à zéro et a est égal à 1; dans ce cas, d est égal à zéro ou est plus grand, e est égal à au moins 1 et f est égal à zéro ou est plus grand,

$Z_1$  à  $Z_7$  sont identiques ou différents et au moins l'un des radicaux  $Z_1$  à  $Z_7$  est une chaîne latérale hydrophile et  $Z_1$  à  $Z_7$  sont choisis dans le groupe comprenant un hydrocarbure monovalent ayant de 1 à 20 atomes de carbone, un hydrocarbure halogéné monovalent ayant de 1 à 20 atomes de carbone et une chaîne latérale hydrophile avec les formules suivantes choisies dans le groupe comprenant:

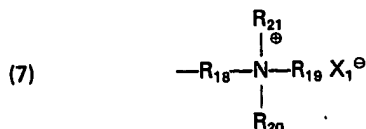


dans laquelle R est un hydrocarbure bivalent ayant de 1 à 10 at m s d carbone,  $R_1$  est choisi dans le

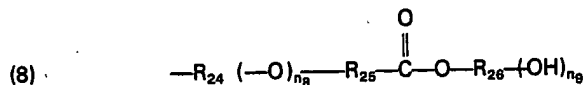
groupe comprenant le méthyle et l'hydrogène, R<sub>2</sub> est choisi dans le groupe comprenant l'hydrogène, un hydr carbure mon valent ayant de 1 à 10 atomes de carbone,



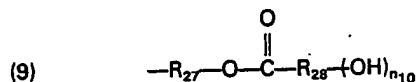
dans laquelle  $R_{16}$  est un hydrocarbure bivalent ou trivalent ayant de 1 à 10 atomes de carbone et l'atome de S n'est pas fixé sur  $R_{16}$  par un atome de carbone aliphatique en position bêta par rapport à l'atome de Si,  $R_{16}$  peut, ou non, être fixé sur  $R_{17}$  pour former un anneau qui contient plus de trois atomes de carbone et  $R_{17}$  est choisi dans le groupe comprenant un hydrocarbure ayant de 1 à 10 atomes de carbone et  $-O^{\ominus} M^{\oplus}$ , où M est choisi dans le groupe comprenant un ion métal monovalent et un ion ammonium quaternaire, et  $n_7$  est égal à 1 ou 2;



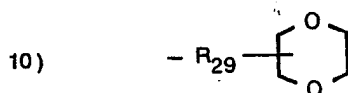
dans laquelle  $R_{18}$  est un hydrocarbure bivalent ayant de 3 à 10 atomes de carbone et le  $N^{\oplus}$  doit être fixé sur un atome de carbone de  $R_{18}$  qui est à au moins deux atomes de carbone de l'atome de Si,  $R_{19}$ ,  $R_{20}$  et  $R_{21}$  sont identiques ou différents et sont des hydrocarbures monovalents ayant de 1 à 10 atomes de carbone,  $X_1^{\ominus}$  est un anion monovalent choisi dans le groupe comprenant les halogénures,  $R_{22}-COO^{\ominus}$ , dans lequel  $R_{22}$  est choisi dans le groupe comprenant l'hydrogène, un hydrocarbure monovalent ayant de 1 à 10 atomes et un hydrocarbure monovalent halogéné ayant de 1 à 10 atomes de carbone, et  $R_{23}-SO_3^{\ominus}$  dans lequel  $R_{23}$  est choisi dans le groupe comprenant un hydrocarbure monovalent ayant de 1 à 10 atomes de carbone et un hydrocarbure monovalent halogéné ayant de 1 à 10 atomes de carbone;



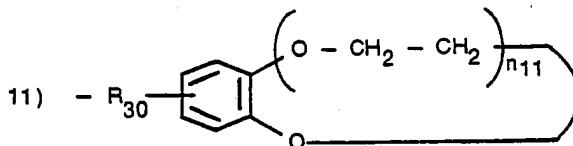
dans laquelle  $R_{24}$  est un hydrocarbure bivalent ayant de 1 à 10 atomes de carbone et  $n_8$  est égal à zéro ou 1 et, quand  $n_8$  est égal à 1, l'oxygène ne peut pas être fixé sur un atome de carbone aliphatique de  $R_{24}$  qui soit en position bêta par rapport à l'atome de Si,  $R_{25}$  est un hydrocarbure bivalent ayant de 1 à 10 atomes de carbone,  $R_{26}$  est un hydrocarbure ayant de 2 à 20 atomes de carbone et une valence de  $n_9 + 1$  et ne peut pas avoir plus d'un atome d'oxygène fixé sur un atome de carbone quelconque et  $n_9$  est égal à au moins 1;



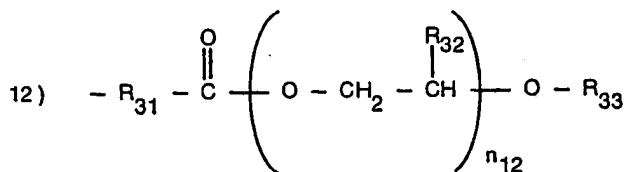
dans laquelle  $R_{27}$  est un hydrocarbure bivalent ayant de 1 à 10 atomes de carbone et l'atome d'oxygène lié à  $R_{27}$  ne peut pas être fixé sur un atome de carbone aliphatique de  $R_{27}$  qui soit en position bêta par rapport à l'atome de Si,  $R_{28}$  est un hydrocarbure ayant de 1 à 20 atomes de carbone et une valence de  $n_{10} + 1$  et ne peut avoir plus d'un atome d'oxygène fixé sur un atome de carbone quelconque, et  $n_{10}$  est un entier égal à au moins 1;



dans laquelle  $R_{29}$  est un hydrocarbure bivalent ayant de 1 à 10 atomes de carbone;



dans laquelle  $R_{30}$  est un hydrocarbure bivalent ayant de 1 à 10 atomes de carbone et  $n_{11}$  est un entier de 1 à 10;



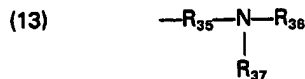
dans laquelle  $R_{31}$  est un hydrocarbure bivalent ayant de 2 à 10 atomes de carbone et le groupe carbonyle

n'est pas fixé sur un atome de carbone en position alpha par rapport à l'atome de Si, R<sub>32</sub> est choisi dans le groupe comprenant le méthyle et l'hydrogène, R<sub>33</sub> est choisi dans le groupe comprenant l'hydrogène, un hydrocarbure monovalent ayant de 1 à 10 atomes de carbone.

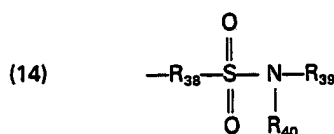
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10 dans lequel  $R_{34}$  est un hydrocarbure monovalent ayant de 1 à 10 atomes de carbone, et  $n_{12}$  est égal à au moins 1;

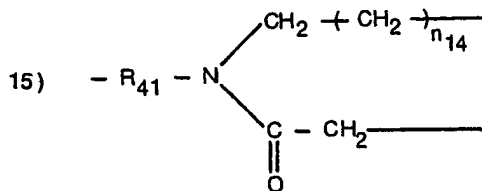


15 dans laquelle  $R_{36}$  est un hydrocarbure bivalent ayant de 1 à 10 atomes de carbone,  $R_{36}$  et  $R_{37}$  peuvent être identiques ou différents et sont choisis dans le groupe comprenant l'hydrogène, des hydrocarbures monovalents ayant de 1 à 10 atomes de carbone et  $-(CH_2)_{n_{13}}-OH$ , où  $n_{13}$  est égal à 2, 3 ou 4;



26 dans laquelle  $R_{38}$  est un hydrocarbure bivalent ayant de 1 à 10 atomes de carbone et l'atome de S ne peut pas être fixé sur un atome de carbone de  $R_{38}$  qui soit en position alpha par rapport à l'atome de Si,  $R_{39}$  et  $R_{40}$  peuvent être identiques ou différents et sont choisis dans le groupe comprenant l'hydrogène et un hydrocarbure monovalent ayant de 1 à 10 atomes de carbone;

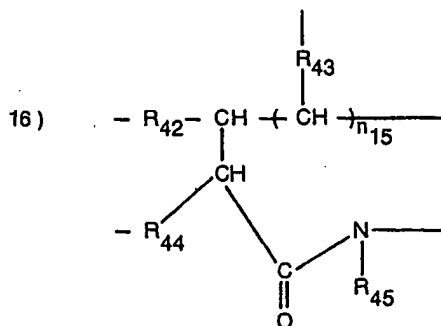
**30**



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dans laquelle  $R_{41}$  est un hydrocarbure bivalent ayant de 1 à 10 atomes de carbone et  $n_{14}$  est égal à 0, 1, 2 ou 3;

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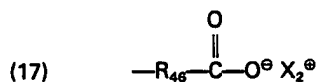


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55 dans laquelle  $n_{15}$  est égal à 0, 1, 2 ou 3,  $R_{42}$  et  $R_{43}$  sont choisis dans le groupe comprenant l'hydrogène, des hydrocarbures bivalents ou monovalents ayant de 1 à 10 atomes de carbone et  $R_{44}$  est choisi dans le groupe comprenant l'hydrogène, des hydrocarbures bivalents ou monovalents ayant de 1 à 10 atomes de carbone et seulement l'un des radicaux  $R_{42}$ ,  $R_{43}$  et  $R_{44}$  doit être un hydrocarbure bivalent et être fixé sur l'atome de Si,  $R_{45}$  est choisi dans le groupe comprenant l'hydrogène, un hydrocarbure monovalent ayant de 1 à 10 atomes de carbone et  $-(CH_2)_{n_{16}}-OH$ , dans lequel  $n_{16}$  est égal à 2, 3 ou 4;

60

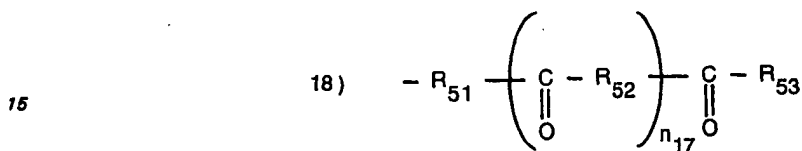


65 dans laquelle  $R_{48}$  est un hydrocarbure bivalent ayant de 2 à 10 atomes de carbone et le radical carbonyle ne

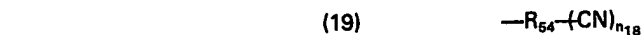
peut pas être fixé sur un atome de carbone en position alpha par rapport à l'atome de Si et  $X_2^\oplus$  est un cation monovalent choisi dans le groupe comprenant des cations métalliques monovalents et



10 dans lequel  $R_{47}$ ,  $R_{48}$ ,  $R_{49}$  et  $R_{50}$  sont identiques ou différents et sont choisis dans le groupe comprenant l'hydrogène et un hydrocarbure monovalent ayant de 1 à 10 atomes de carbone;

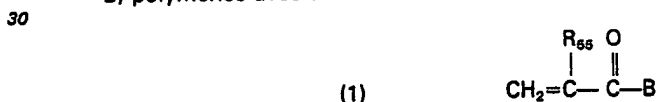


20 dans laquelle  $R_{51}$  est un hydrocarbure bivalent ayant de 1 à 10 atomes de carbone et le radical carbonyle ne peut pas être fixé sur un atome de carbone en position alpha par rapport à l'atome de Si,  $R_{52}$  est un hydrocarbure bivalent ayant de 1 à 10 atomes de carbone,  $R_{53}$  est choisi dans le groupe comprenant l'hydrogène et un hydrocarbure monovalent ayant de 1 à 10 atomes de carbone, et  $n_{17}$  est un entier de zéro à 10, et

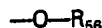


dans laquelle  $R_{54}$  est un hydrocarbure ayant de 1 à 20 atomes de carbone et ayant une valence de  $n_{18} + 1$  et aucun radical  $-\text{C} \equiv \text{N}$  n'est fixé sur un atome de carbone de  $R_{54}$  qui soit en position alpha par rapport à l'atome de Si et  $n_{18}$  est un entier supérieur à zéro;

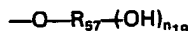
B) polymérisé avec un comonomère choisi dans le groupe comprenant:



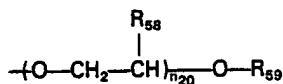
35 dans lequel  $R_{55}$  est choisi dans le groupe comprenant l'hydrogène et le méthyle et B est choisi dans le groupe comprenant



40 dans lequel  $R_{56}$  est choisi dans le groupe comprenant l'hydrogène et un hydrocarbure monovalent ayant de 1 à 20 atomes de carbone,



45 dans lequel  $R_{57}$  est un hydrocarbure ayant de 2 à 20 atomes de carbone et une valence de  $n_{19} + 1$  et ne peut pas avoir plus d'un atome d'oxygène fixé sur un atome de carbone quelconque et  $n_{19}$  est un entier supérieur à zéro,



50 dans lequel  $R_{58}$  est choisi dans le groupe comprenant l'hydrogène et le méthyle,  $R_{59}$  est choisi dans le groupe comprenant l'hydrogène, un hydrocarbure monovalent ayant de 1 à 20 atomes de carbone, le radical



dans lequel  $R_{60}$  est un hydrocarbure monovalent ayant de 1 à 20 atomes de carbone et  $n_{20}$  est un entier supérieur à zéro,



65 dans lequel  $R_{61}$  et  $R_{62}$  sont identiques ou différents et sont choisis dans le groupe comprenant l'hydrogène,

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un hydrocarbure monovalent ayant de 1 à 20 atomes de carbone et  $-(CH_2)_{n_2}D$ , où D est choisi dans le groupe comprenant  $-OH$  et

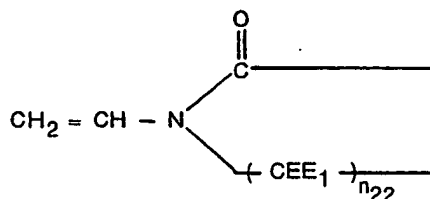


dans lequel  $R_{63}$  et  $R_{64}$  sont identiques ou différents et sont de l'hydrogène ou des hydrocarbures monovalents ayant de 1 à 20 atomes de carbone et  $n_{21}$  est égal à 2 ou 3,

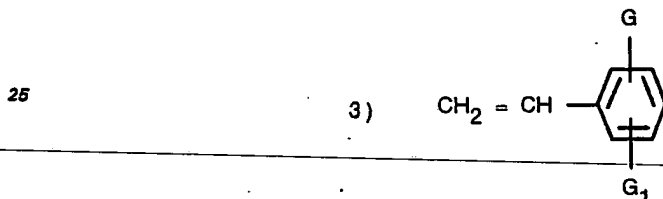
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2)



20 dans lequel E et  $E_1$  sont identiques ou différents et sont choisis dans le groupe comprenant l'hydrogène et un hydrocarbure monovalent ayant de 1 à 10 atomes de carbone et  $n_{22}$  est égal à 2, 3, 4 ou 5,



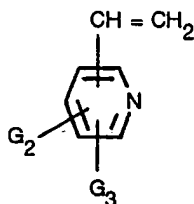
30 dans lequel G et  $G_1$  sont identiques ou différents et sont choisis dans le groupe comprenant l'hydrogène, un halogène, un hydrocarbure monovalent ayant de 1 à 20 atomes de carbone, un radical hydroxyle,



40 où  $R_{65}$  et  $R_{66}$  sont identiques ou différents et sont choisis dans le groupe comprenant l'hydrogène et un hydrocarbure monovalent ayant de 1 à 20 atomes de carbone,

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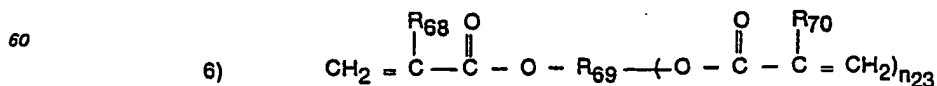
4)



50 dans lequel  $G_2$  et  $G_3$  sont identiques ou différents et sont choisis dans le groupe comprenant l'hydrogène et un hydrocarbure monovalent ayant de 1 à 10 atomes de carbone,

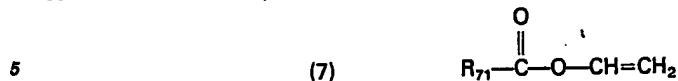


dans lequel  $R_{67}$  est choisi dans le groupe comprenant l'hydrogène et le méthyle,

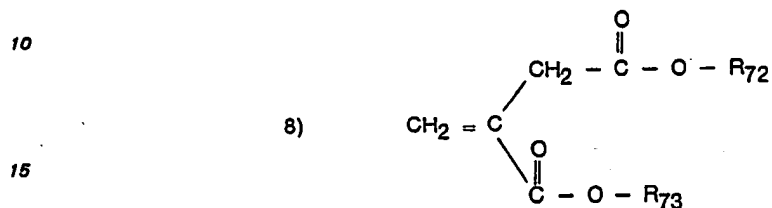


65 dans lequel  $R_{68}$  et  $R_{70}$  sont identiques ou différents et sont choisis dans le groupe comprenant l'hydrogène

et le méthyle,  $R_{69}$  est un hydrocarbure ayant de 1 à 20 atomes de carbone et une valence de  $n_{23} + 1$  et  $n_{23}$  est un entier de 1 à 5,



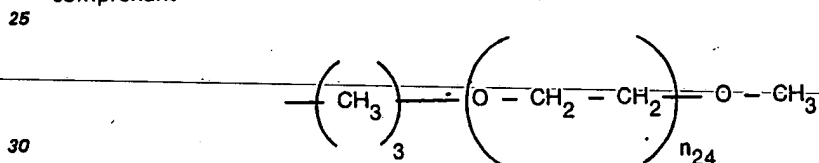
dans lequel  $R_{71}$  est un hydrocarbure monovalent ayant de 1 à 20 atomes de carbone, et



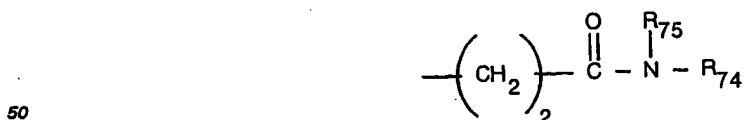
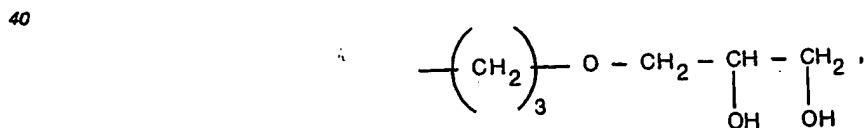
dans lequel  $R_{72}$  et  $R_{73}$  sont identiques ou différents et sont choisis dans le groupe comprenant l'hydrogène et un hydrocarbure monovalent ayant de 1 à 20 atomes de carbone,

20 C) ce polymère étant formé en un réseau réticulé pouvant, lorsqu'il est saturé par de l'eau, retenir d'environ 1 à environ 99% en poids d'eau, sur la base du poids total du polymère et de l'eau.

2. Objet selon la revendication 1, dans lequel la chaîne latérale hydrophile est choisie dans le groupe comprenant



dans lequel  $n_{24}$  est égal à 2 ou 3,

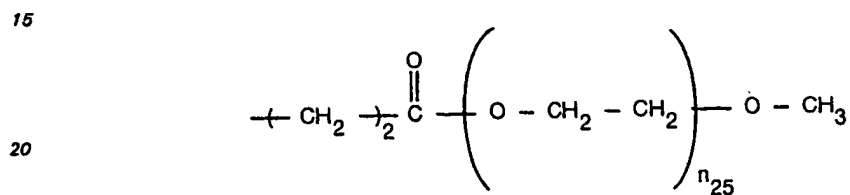
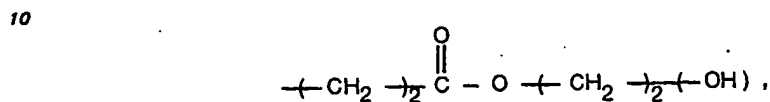


dans lequel  $R_{74}$  et  $R_{75}$  sont identiques ou différents et sont choisis dans le groupe comprenant l'hydrogène, le méthyle et  $-\text{CH}_2-\text{CH}_2-\text{OH}$ ,

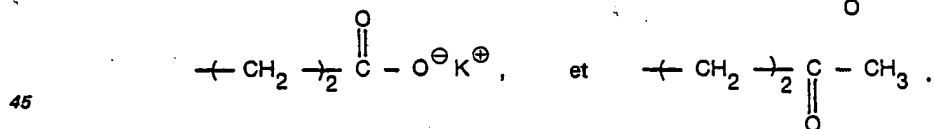
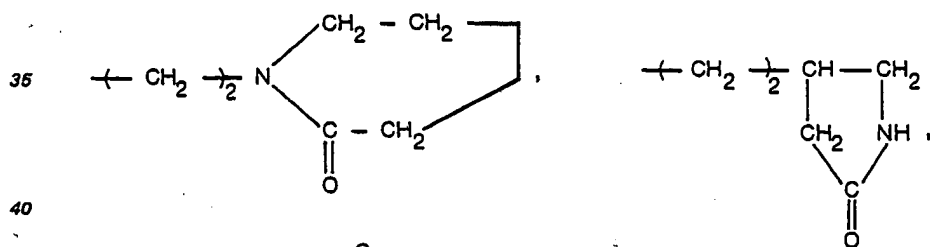
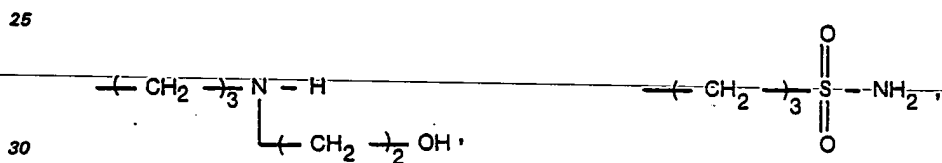


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dans lequel  $R_{76}$  est choisi dans le groupe comprenant l'hydrogène et le méthyle,



dans lequel  $n_{25}$  est égal à 2 ou 3,



3. Objet selon la revendication 1 ou 2, dans lequel X est choisi dans le groupe comprenant



dans lequel  $n_{26}$  est un entier de 1 à environ 10,

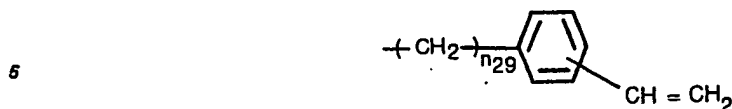


dans lequel  $n_{27}$  est un entier de 1 à environ 10,





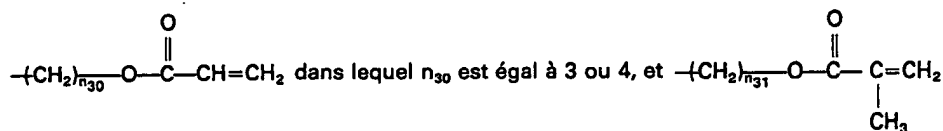
dans lequel  $n_{28}$  est un entier de 1 à environ 10,



dans lequel  $n_{29}$  est un entier de 0 à environ 10.

4. Objet selon la revendication 3, dans lequel X est choisi dans le groupe comprenant

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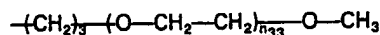
dans lequel  $n_{31}$  est égal à 3 ou 4.

5. Objet selon l'une quelconque des revendications précédentes, dans lequel l'un seulement des radicaux  $Z_1$ ,  $Z_2$ ,  $Z_5$  et  $Z_6$  est une chaîne latérale hydrophile.

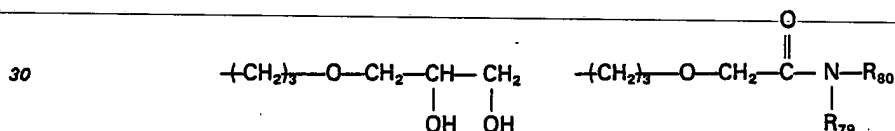
20 6. Objet selon la revendication 5, dans lequel  $a$  est égal à environ 10 à 500,  $b$  est égal à zéro,  $c$  est égal à 1,  $d$  est égal à environ 10 à 500,  $e$  est égal à 1 et  $f$  est égal à zéro.

7. Objet selon la revendication 6, dans lequel  $Z_1$ ,  $Z_2$  et  $R_5$  sont des radicaux méthyle et  $Z_6$  est choisi dans le groupe comprenant

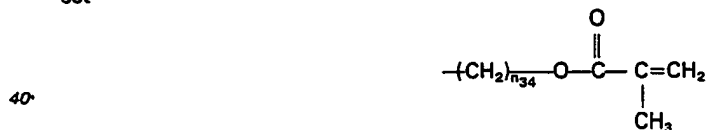
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dans lequel  $n_{33}$  est égal à 2 ou 3,



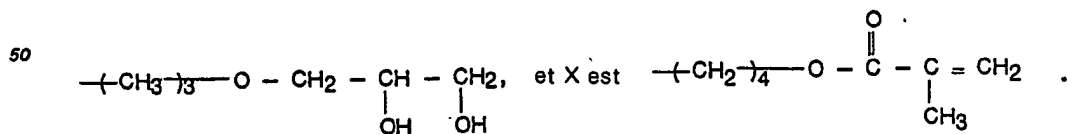
35 dans lequel  $R_{79}$  est choisi dans le groupe comprenant le méthyle et l'hydrogène,  $R_{80}$  est choisi dans le groupe comprenant le méthyle, l'hydrogène et  $\text{-CH}_2\text{-CH}_2\text{-OH}$ ,  $Y_1$  et  $Y_2$  sont des radicaux méthyle et X est



dans lequel  $n_{34}$  est égal à 3 ou 4.

45 8. Objet selon l'une quelconque des revendications 1 à 4, dans lequel seulement l'un des radicaux  $Z_1$  à  $Z_7$  est une chaîne latérale hydrophile.

9. Objet selon la revendication 8, dans lequel  $Z_1$ ,  $Z_2$ ,  $Z_3$ ,  $Z_6$ ,  $Y_1$  et  $Y_2$  sont des radicaux méthyle,  $Z_3$  et  $Z_4$  sont de l'hydrogène et  $Z_7$  est



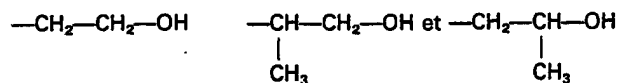
55 10. Objet selon l'une quelconque des revendications précédentes, dans lequel le comonomère est



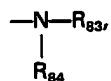
dans lequel  $R_{81}$  est choisi dans le groupe comprenant l'hydrogène et le méthyle, et B est  $\text{-O-R}_{82}$ , dans lequel  $R_{82}$  est choisi dans le groupe comprenant un hydrocarbure monovalent ayant de 1 à 12 atomes de carbone, un dérivé d'hydrocarbure monovalent ayant de 1 à 12 atomes de carbone et l'hydrogène.

65

11. Objet selon la revendication 10, dans lequel  $R_{82}$  est choisi dans le groupe comprenant

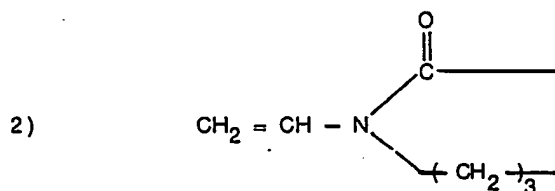


12. Objet selon la revendication 10 ou la revendication 11, dans lequel B est



dans lequel  $R_{83}$  et  $R_{84}$  sont identiques ou différents et sont choisis dans le groupe comprenant l'hydrogène, le méthyle et  $\text{---CH}_2\text{---CH}_2\text{---OH}$ .

13. Objet selon l'une quelconque des revendications 1 à 9, dans lequel le comonomère est



14. Objet selon l'une quelconque des revendications précédentes, qui est une lentille de contact absorbant l'eau, molle, hydrophile, souple, hydrolytiquement stable et biologiquement inerte avec un potentiel de transport d'oxygène suffisant pour satisfaire les exigences de la cornée humaine.